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Methods of Removing Uranium From Drinking Water

I. A Literature Survey

II. Present Municipal Water Treatment and Potential Removal Methods

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Information Division

METHODS OF REMOVING URANIUM FROM DRINKING WATER.

I. A LITERATURE SURVEY.

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Health and Environmental Studies Program
Information Center Complex

II. PRESENT MUNICIPAL WATER TREATMENT AND POTENTIAL REMOVAL METHODS

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METHODS OF REMOVING URANIUM FROM DRINKING WATER: I. A LITERATURE SURVEY

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ABSTRACT

Literature was searched for methods of removing uranium from drinking water. No relevant papers were found, but approximately 1000 publications were identified in a less specific search for methods of removing uranium from water. Most of the latter publications dealt with the recovery of uranium from ores, industrial and analytical chemistry solutions, or seawater. The conditions under which these studies were performed were usually quite different from those normally occurring in municipal water treatment practice, but some potentially interesting systems of recovery were identified. A few papers addressed the problem of removing uranium from natural fresh waters and established the effectiveness of using adsorbents or coprecipitants, such as aluminum hydroxide, ferric hydroxide, activated carbon, and ion exchangers, under certain conditions. Also, many U.S. manufacturers and users of water treatment equipment and products were contacted regarding recommended methods of removing uranium from potable water. Based on the results of these surveys, it is recommended that untreated, partially treated, and finished water samples from municipal water treatment facilities be analyzed to determine their extent of removal of uranium by presently used procedures. In addition, laboratory studies are suggested to determine what changes, if any, are needed to maximize the effectiveness of treatments that are already in use in existing water treatment plants.

1. INTRODUCTION

This survey was prepared by members of the Health and Environmental Studies Program (HESP), Information Division, Oak Ridge National Laboratory, for the Office of Drinking Water (ODW), U.S. Environmental Protection Agency, to identify technically and economically feasible methods of removing uranium from drinking water and to indicate problem areas requiring additional investigation. The survey is part of a larger ODW program to determine the occurrence of uranium in U.S. surface and groundwaters. This report is based on extensive contacts with suppliers of water treatment equipment and products and on computer searches of the following data bases: Chemical Abstracts (1972-80), Nuclear Science Index (1967-76), National Uranium Resource Evaluation (1945-79), Environmental Aspects of Transuranics (1945-78), Chemical Industry Notes (1974-80), Compendex (1970-80), Metadex (1966-79), and Current Research (1978-79).

Searches of the above data bases were unproductive when the search strategy limited the scope of the search to "drinking" water, but approximately 1000 publications were identified when the less restrictive search descriptor, "water," was used. In general, most of these publications concerned the recovery of uranium from water under very special circumstances, such as the extraction of uranium from ores or industrial processing solutions and wastewaters, from seawater, or from solutions used in analytical chemistry. The greater portion of the cited publications was not directly applicable to the present study, because boundary conditions and objectives were drastically different from conditions in potable water systems. Pertinent characteristics of many of these systems have been summarized in Table 1, and the most interesting methods are briefly discussed in Sects. 2, 3, and 4. Techniques deemed more attractive for use in potable water systems are discussed in Sect. 5, and recommendations for future research are made in Sect. 6.

2. REMOVAL OF URANIUM FROM ORES OR INDUSTRIAL PROCESS SOLUTIONS, INDUSTRIAL WASTEWATERS, AND MINE EFFLUENTS

The advent of the Atomic Age in the early 1940s provided the impetus for the hitherto neglected study of uranium chemistry in general and for the development of specific methods for recovering uranium from aqueous solutions. During the subsequent three decades, hundreds of papers were published describing precipitation, solvent extraction, and ion exchange techniques applicable to uranium-rich process streams, uranium-depleted waste streams, and uranium-mine effluents. Many of these papers were described at one of the three International Conferences on the Peaceful Uses of Atomic Energy held in Geneva between 1955 and 1964 (Bruce et al., 1956; Bruce, Fletcher, and Hyman, 1958; Bruce, Fletcher, and Hyman, 1961; Stevenson, Mason, and Gresky, 1970). More recently, uranium has been removed from aqueous process streams, wastewaters, and mine effluents by countercurrent ion exchange (George and Rosenbaum, 1970; Ross and George, 1971), ion exchange membranes (Davis, Wu, and Baker, 1971), organic phosphates (Peppard et al., 1973; Tsujino et al., 1970), trioctylphosphine oxide (Konstantinova and Mareva, 1977), polyacrylamidosalicyclic acid (Kennedy et al., 1973), alkyl ammonium compounds (Sato, Kotani, and Good, 1974; Juenger and Schmidt, 1974), ion flotation (Jude and Fratila, 1974; Zivanov, Miskovic, and Karlovic, 1977), bone char (Blane and Murphy, 1976), various types of coal (Cameron and Leclair, 1975), and biological sorbents such as fungi, yeasts, and bacteria (Jilek, Fuska, and Nemec, 1978; Shumate, Strandberg, and Parrott, 1979). Typical examples of the systems listed above are characterized in Table 1.

It can be seen from Table 1 that most of the listed adsorption, solvent extraction, and ion exchange systems removed 90% or more of the initial uranium from the processed solutions. In many instances, however, the initial uranium concentrations were so great that even processes having removal efficiencies greater than 90% still produced effluents containing as much as 1000 ppb uranium. Concentrations of this degree are unacceptably high for drinking water. If these processes were operated with feedstocks containing much lower concentrations of uranium (similar to those of certain western municipal water treatment plants), some uranium removal

Table 1. Pertinent characteristics of selected systems for removing uranium from industrial processing solutions, analytical chemistry solutions, and seawater

Process	Extractant, reagent, or resin: Name	Extractant, reagent, or resin: Toxicity problem?	Operating conditions: Initial reagent concentration	Operating conditions: Initial pH	Operating conditions: Initial uranium concentration (mg/L)	Operating conditions: Concentration of uranium in effluent (ug/L)	Operating conditions: Uranium removed (%)	Operating conditions: Decontamination factor	Comments	Reference
Adsorption	Lignite	No		2.65	155	<1000	99.4			Cameron and LeClair, 1975
	Coke	No		2.65	155	<1000	99.4			Cameron and LeClair, 1975
	Charcoal	No	0.1 mg/mL	5 - 8	0.0025		~100		0.75 mg/mL L-ascorbic acid added before extraction	Van Der Sloot, Massee, and Das, 1975
	Penicillomyces marquandii	No	1.2 g/L, dry		20	1200	94			Shumate, Strandberg, and Parrott, 1979
	Saccharomyces cerevisiae	No	1.2 g/L, dry		20	1000	95			Shumate, Strandberg, and Parrott, 1979
	Pseudomonas aeruginosa	No	1.2 g/L, dry		20	1600	92			Shumate, Strandberg, and Parrott, 1979
	Unicellular green algae	No			0.006	<6		>1000 accumulation factor		Heide and Wagener, 1973
	Aspergillus niger	No			0.006				Dry fungal mass contained 10 - 40 mg U/kg	British patent 1,507,003, 1979
	Silica gel	No		6	0.003		90 - 100			Petrol and Schwoschau, 1978
	Hydrous titanium oxide	No			0.003		High			Kees, 1977
	Titanium hydroxide	No		8	0.003		33 - 70			Davies, Flannedy, McIlroy, and Spence, 1964 (see also Kanno, 1977)
	Galena	No		8	0.003		80 - 95			Koyanaka, 1970
	Polyacrylamide gel containing titanium hydroxide	No		7.8	0.003		80			Shigetomi, Kojima, and Shimagawa, 1977
	Bone char	No		6.5 - 7.5	11	4	66	3.0		Blase and Murphy, 1976
	Composite hydrous titanium(IV)-iron(II) oxide	No	40 mg/L	8	0.010		24			Ozawa, Murata, Yamashita, and Nakajima, 1979
	Titanium/arsenic compound	Possibly	2 mg/L	8	0.003		28			Murata, T., 1974
Electrolysis	Magnesium hydroxide	No			0.003		0.1 mg U/g deposited magnesium hydroxide		Seawater	Wooten, Hirayama, Paxton, and Patton, 1976
Froth flotation	Aerosol 111-Zephiramine	Possibly			0.003		98			Sekine, 1975
	Ferric hydroxide	No	0.3 mM	6.7	0.004 - 0.012		87		Sodium dodecyl sulfate added before extraction	Kim and Zeitlin, 1971
	Hydrated titanium oxide	No		6.6	0.00 - 40.012		91		Sodium dodecyl sulfate added before extraction	Williams and Gillam, 1978
	Amines, aeroflaat, fatty acids	No		3 - 8	2 - 5		87 - 95			Jude and Fratila, 1974
	Thorium hydroxide		0.4 mM	5.7	0.004 - 0.012		90		Sodium dodecanate added	Leung, Kim, and Zeitlin, 1972
	Dimethyldistearyl-ammonium chloride	No	42 mg/L	7	50		High			Zivanov, Miskovic, and Karlovic, 1977
Ion exchange membrane	AMF-ion C-103	No			1940	130,000	96			Davis, Wu, and Baker, 1971
Ion exchange resin	Functional group 1-(2-hydroxyphenylazo)-2-naphthol	No		3	0.010		89			Burba and Lieser, 1977
	Arsenic acid	No	5	5	0.5		~100		0.01 *M* EDTA added before extraction	Fritz and Moyers, 1976
	RA400	No		Alkaline	1000	1000	99.9			Josephson, 1976
	Strong base anion exchanger	No		Alkaline	9 - 12	100	97.5 - 99			Ross and George, 1971
	Strong base anion exchanger	No			0.025 - 10.0	~0	~100		Ascorbic acid and potassium thiocyanate added to complex uranium	Korkisch and Godl, 1974

Table 1 (continued)

Process	Extractant, reagent, or resin		Operating conditions						Comments	Reference
	Name	Toxicity problem?	Initial reagent concentration	Initial pH	Initial uranium concentration (mg/L)	Concentration of uranium in effluent (μg/L)	Uranium removed (%)	Decontamination factor		
Liquid anion exchange	Amberlite LA-1 [N-dodecyl(trimethyl)amine]	No	4% in xylene	2.5–4.0	5.18		99.1		0.001 *M* malonic acid added	Dalvi and Khopkar, [illegible] '78
Partial precipitation	Sodium hydroxide	No	3.5 mg/L	8	0.006		68			Hodge, Hoffman, Foreman, and Folsom, 1954
Precipitation	Hydrogen sulfide	Possibly	800 mg/L	6–6.5	50–100	100	99.9			Kochanov, Korolev, Dubinchuk, and Medvedev, 1977
Reverse osmosis	Cellulose acetate membrane	No			100–8000		98–99.4		250 psig, uranyl sulfate solutions	Sastri and Ashbrook, 1976
		No			30	<500			250 psig, synthetic mine water	Sastri and Ashbrook, 1976
Solvent extraction	Aliquot-336	No	0.1 *M* in diethyl-benzene	0.2 *M* HCl	0.003	~0	~100		3.5 *M* lithium chloride added	Barbano and Rigali, 1978
	Polymer-bound macro-cyclic hexaketone	Possibly	0.1 mmol in 3.0 ml chloroform	8	0.003		36			Tabushi, Kobuke, and Nishiya, 1979
	Caprylohydroxamic acid	Possibly	0.5% w/v in 1-hexanol	8	10		~100			Vernon and Khorasani, 1978
	N,N-Di-n-octylacetamide	Possibly	1 *M* in chloroform	9 *M* HCl				788 (organic/aqueous distribution ratio)		Fuhlandt and Fritz, 1979
	Di-n-butyl phosphate	Possibly					>99			Tajima, Aoshi, Hoshino, and Muman, 1970
		Possibly			0.003		~100			Stanton, 1953
	Trioctylphosphine oxide	Possibly		4.7–5.5			93			Konstantinova and Mazova, 1977
	Poly(4- and 5-acrylamido salicylic acid)	Possibly		1.3–9.0	100–1000		~100			Kennedy, Barker, Nicol, and Hawkins, 1973
	Tricaprylmethylammonium chloride	Possibly	0.02 *M* in benzene	0.15 *M* HCl	700			17 (organic/aqueous distribution ratio)	0.5 *M* potassium thiocyanate added. Uranium extracted as uranyl thiocyanate complex	Sato, Kotani, and Good, 1974
	Di(2-ethylhexyl)-phosphoric acid plus trioctyl-phosphoric oxide	Possibly	0.5 *M* in Amsco 450	5–6 *M* H_3PO_4	140–190	7–9.5	95			Hunt, Crouse, and Brown 1972
Ultrafiltration	Hollow fiber membranes	No							Good for suspended or colloidal, but not for dissolved uranium	Roberts and Koenst, 1977

would still probably occur, but decontamination efficiencies would change and laboratory studies based on the new conditions would be needed to determine the technical feasibility of the processes.

It should also be noted here that a process can remove uranium efficiently and still not be a practical or economical municipal water treatment procedure. In addition to the efficiency of the removal of uranium, the major considerations are capital and operating costs (Sorg and Logsdon, 1980). If a new treatment process can be added to an existing plant with minimum modifications or changes in operation, only small increases in capital and operating costs may occur. If a new treatment process cannot fit into an existing system without major changes, substantial capital costs will be incurred in constructing a new facility, and increased costs may be incurred in its operation. Based on these considerations, adsorption processes are the most interesting of all the uranium-removing techniques listed in Sect. 2 of this report. Virtually all municipal water treatment facilities that process surface waters already have in use the contactors and filters needed in the removal of uranium by the adsorption technique, and necessary modifications may be effected with minimum incremental cost. However, municipal water treatment plants that process groundwaters frequently do not have such facilities; nevertheless, the equipment is commercially available, and the general technology is well established. Coal, coke, lignite, bone char, and hydrated titanium oxide or hydroxide are potentially interesting as uranium-removing adsorbents, but data concerning their uranium-removing efficiencies under typical municipal water plant operating conditions are needed before a critical selection can be made.

Ion exchange processes constitute the second most interesting group of uranium-removing techniques listed in Sect. 2. Although it is not evident from the data in Table 1, there is no technological difficulty in reducing uranium in processed water to any desired concentration by treatment with appropriate ion exchange resins (Higgins, 1980). In acid waters where uranium exists as the uranyl ion, cation exchangers must be used; for natural waters containing carbonate, where uranium occurs as the $[UO_2(CO_3)_3^{4-}]$ complex, anion exchangers are needed. However, impurities in the processed water can interfere with the intended operation of

ion exchange systems, loading the resin with an undesired adsorbent, decreasing resin capacity for uranium, and increasing the cost of regenerating the resin. In addition, the use of ion exchangers in the treatment of municipal waters usually involves relatively high capital costs. For these reasons ion exchange is used only rarely in municipal water treatment systems that process surface water (Sorg and Logsdon, 1980). In groundwater treatment plants, cation and anion exchangers are sometimes used to remove hardness (calcium and magnesium ions) and nitrates. Whether or not ion exchange techniques should be incorporated into municipal water treatment plant procedures for the purpose of removing uranium is thus primarily an economic question that depends to a considerable extent on the composition of the water to be treated.

The solvent extraction techniques listed in Sect. 2 and Table 1 generally have high uranium extraction efficiencies and can be used to deplete uranium in certain effluents to very low levels. However, as a class, solvent extraction methods are not well suited to the removal of uranium from drinking water. In general, these two-phase, liquid-liquid extraction systems require specialized contacting equipment that is not normally found in conventional municipal water treatment systems. Furthermore, because of the large throughput of most municipal water treatment plants, the contacting equipment must be large and thus relatively expensive. Although aqueous-organic extraction systems are usually designed for minimum miscibility of the two phases, the aqueous phase usually contains measurable amounts of the organic solvent or the reagent, or both. Typically, both reagent and organic solvent are undesirable drinking water components. Removal of these trace impurities may be troublesome and expensive. Consequently, solvent extraction techniques are seldom used in municipal water treatment procedures. Their usage in the removal of uranium from drinking water should be considered only in the absence of other more appropriate techniques.

3. REMOVAL OF URANIUM FROM SEAWATER

Seawater contains about 3.3 μg/L uranium or an approximate total of 4.5 billion metric tons (Rodman, Gordon, and Chen, 1979). During the last 10 years, an anticipated shortage of uranium reserves has stimulated extensive research into methods of recovering uranium from seawater. This research is being done primarily in Japan, West Germany, England, and Russia. Proposed methods include phosphate precipitation (Yamabe and Takai, 1970), electrochemical deposition (Shigetomi, Kojima, and Shinagawa, 1976; Wooten et al., 1976), anion exchangers (Ryabinin, Lazareva, and Doroshenko, 1973), and various colloidal flotation schemes (Barannik et al., 1976; Kim and Zeitlin, 1971; Zhorov et al., 1976). Adsorption of uranium on various substrates has also been frequently suggested, for example, on: hydroxylapatite (Takai, Takase, and Yamabe, 1971), surfactants (Ogata and Kakihana, 1969), galena (Koyanaka, 1970; Mukai and Koyanaka, 1974), peat or brown coal (Astheimer, Schenk, and Schwochau, 1978; Wilhelms, 1972; Heitkamp and Wagener, 1977), macrocyclic hexaketone (Tabushi, Kobuke, and Nishiya, 1979), benzimidazole polymer (Taniguchi, Nakayama, and Tani, 1978), hippuric acid formaldehyde copolymer (Taniguchi, Nakayama, and Tani, 1978), hydrous metal oxides or hydroxides (Ozawa et al., 1979; Ninomiya, Sugasaka, and Fujii, 1971; Shigetomi, Kojima, and Shinagawa, 1976; Okamoto Yamaguchi, and Takahashi, 1979), silica gel (Ito, Yamazaki, and Kantake, 1977; Putral and Schwochau, 1978), chelating resins and fibers (Egawa and Harada, 1979), quinaldic acid resin (Sakamoto and Tani, 1977), and various microorganisms such as algae, fungi, and bacteria (Heide et al., 1973; Horikoshi, Nakajima, and Sakaguchi, 1979; Jilek et al., 1974). Additional papers on methods of removing uranium from seawater are contained in reviews by Keen (1977), Ogata (1976), Miyazaki (1977), and Novikov and Lipova (1976) and in bibliographies by Khan and Saleem (1973) and Chen et al. (1979). Operating conditions and uranium extraction efficiencies for the most relevant systems listed above are given in Table 1.

Of the various methods proposed for recovering uranium from seawater there is substantial agreement in the field that retention of dissolved uranium on a fixed adsorbent is likely to be the most efficient and cost effective technique. Hydrated metal oxides or hydroxides and certain

functional groups in the cellular walls of microorganisms appear to offer potentially attractive adsorptive sites. Among metal hydroxide adsorbents, hydrous titanium (IV) oxide or titanium hydroxide seems more attractive than hydroxides of other elements (Llewelyn, 1976; *Technology Newsletter*, 1980; Kanno, 1977; Davies et al., 1964). The technological attractiveness of titanium hydroxide stems from its availability, low unit cost, relative insolubility in seawater, and high uptake capacity for uranium. Titanium hydroxide prepared by neutralizing titanium sulfate with an alkali adsorbs 760 µg uranium per gram of titanium, but other methods of preparation, such as the thermal decomposition of titanium sulfate, can more than double this uranium uptake (Kanno, 1977). Based on these favorable characteristics, the Metal Mining Agency of Japan decided to authorize the construction of a $6.2 million pilot plant based on the use of a titanium hydroxide adsorbent. Construction of the pilot plant, which will be designed to produce 10 kg of uranium per year, will begin in the latter part of 1980 (*Technology Newsletter*, 1980).

Despite the relative advantages of titanium hydroxide over other metal hydroxide adsorbents in the recovery of uranium from seawater, its application for this purpose now is not economically competitive with existing commercial methods of producing uranium (Harrington et al., 1974), nor is its use expected to contribute significant amounts of uranium to the world's stockpile in the near future (Llewelyn, 1976). Koske (1979) and Rodman, Gordon, and Chen (1979) discuss various design and siting problems associated with production facilities that use titanium hydroxide adsorbents for recovering uranium from seawater.

Of the various adsorbents listed in this section, peat, coal, hydrous metal oxides, and microorganisms, such as *Paecilomyces marquandii*, *Saccharomyces cerevisiae*, and *Pseudomonas aeruginosa*, appear to have the greatest potential for removing uranium economically from municipal water supplies, but more data are needed concerning extraction efficiencies, loading characteristics, cycling life, and effects of impurities under typical municipal water treatment plant conditions before any firm recommendation can be made.

4. REMOVAL OF URANIUM FROM AQUEOUS ANALYTICAL CHEMISTRY SOLUTIONS

Analytical chemists remove uranium from aqueous solutions by a variety of techniques, the most important of which are precipitation, solvent extraction, and ion exchange. In general these methods are similar to those discussed in Sect. 2 of this report, except that greater emphasis is attached to reagent selectivity, convenience, or speed and less to reagent costs and other factors affecting the economics of the process.

Much of the early work in this field is described by Steele and Taverner (1959), Kraus and Nelson (1956), Peppard (1961), Faris and Buchanan (1966), Korkisch (1966), O'Laughlin (1966), Morrow (1970), and Freiser (1970). More recently uranium has been removed from aqueous analytical chemistry solutions by partial precipitation with alkali (Hodge et al., 1974); extraction with trioctylphosphine oxide (Deutscher and Mann, 1977), Arsenazo III (Keil, 1979), tributyl phoshate (Gorbushina et al., 1972), and ammonium pyrrolidinecarbodithioate (Pradzynski, Henry, and Draper, 1976); adsorption on chelating resins (Hathaway and James, 1975), anion exchangers (Brits and Smit, 1977; Ryabinin, Lazareva, and Doroshenko, 1973), silica gel (Putral and Schwochau, 1978), and activated charcoal (Kuleff and Kostadinov, 1978); electrochemical procedures (Hodge, 1975; Shigetomi, Kojima, and Shinagawa, 1976); various flotation processes (Barannik et al., 1976; Kim and Zeitlin, 1971; Zhorov et al., 1976); and reverse osmosis through cellulose acetate membranes (Sastri and Ashbrook, 1976). Operating conditions and extraction efficiencies for typical analytical chemistry methods are shown in Table 1.

The preceding list of techniques used by analytical chemists to remove uranium from aqueous solutions includes some potentially interesting methods not previously considered. Partial precipitation with sodium hydroxide (Hodge et al., 1974) is less effective than other removal methods (~68% uranium removal from spiked seawater) but is a technique that is compatible with equipment existing in most present-day municipal water treatment plants that use surface water sources. The method should be examined for effectiveness under municipal water treatment plant conditions.

Reverse osmosis, sometimes called hyperfiltration, can also remove uranium from water. In the cited literature, initial concentrations of

100 to 8000 mg/L uranyl sulfate were reduced 98 to 99.4% using cellulose acetate membranes and 1786 kPa (250 psi) pressure. Similarly, synthetic mine effluents containing 30 mg/L uranium were reduced to <500 µg/L. Uranium concentrations of the order of 500 µg/L are unacceptably high for drinking water, but presumably this concentration could be further reduced if this were an operational objective. For example, normal operation of one full-scale reverse osmosis plant reduced the concentration of radium-226 from 3.4 to 0.26 pCi/L (Sorg and Logsdon, 1980). This 92% removal of radium-226 was accomplished while producing 1,000,000 gallons per day of finished water. Obviously, more data are needed to define the efficiency of reverse osmosis systems with respect to the removal of uranium in the ppb range, but there appears to be little doubt that the method is technically capable of lowering the concentration of uranium in treated water. Whether or not reverse osmosis is economically attractive for this purpose must be determined on a case by case basis. In general, reverse osmosis is not economically competitive with conventional municipal water treatment procedures for processing nonsaline feedstocks (Kremen, 1979) but may have lower combined capital and operating costs than distillation, freezing, or electrodialysis methods in producing potable water from brackish water or seawater (Buros, 1979; Larson and Leitner, 1979). Reverse osmosis units are available in a variety of sizes. Some are suitable for individual household use (Mgren, 1980).

Another membrane process, electrodialysis, should also receive consideration as a method of removing uranium from drinking water. No literature reports were found describing the efficiency of this method in removing uranium from drinking water, but general considerations lead to the expectation of a decontamination potential similar to that of the reverse osmosis technique. Electrodialysis systems are commercially available in a variety of sizes; some electrodialysis units are suitable for individual household use (Spiegler, 1977). For several years some highway rest stops and service areas, such as those located at Mohawk and Sentinel, Arizona, and Junius Ponds, New York, have successfully used small, unattended, automatic, electrodialysis units to supply potable water from feedstocks containing high concentrations of calcium sulfate (Goldstein, 1979; Katz, 1979).

Although electrodialysis and reverse osmosis are increasingly used for desalting seawater and brackish groundwaters, neither process can be used on turbid surface waters without extensive pretreatment; consequently, the economic feasibility of using these methods depends on feed water composition and must be determined on a case by case basis.

5. REMOVAL OF URANIUM FROM NATURAL FRESH WATERS

Publications dealing with the removal of uranium from natural fresh waters have greater relevance to the task at hand than do publications mentioned in the previous sections of this report, particularly if the research focused on problems associated with decontamination of water rather than on the recovery of uranium values. Although few reports have been published from this perspective, several papers were found that contain pertinent quantitative data.

In the first of these papers, Weissbuch, Cotrau, and Velicescu (1969) discuss the removal of uranium, cesium-137, strontium-90, and yttrium-90 from laboratory prepared aqueous solutions by the addition of varying amounts of aluminum sulfate and/or activated carbon, followed by mixing, settling, and filtration through fine porosity filter paper. The change in concentration of radioactive elements following this treatment was determined by measuring the initial and final radioactivity of each solution. Decontamination factors were computed on the basis of reduced radioactivity. The authors reported removal of 49% of the initial uranium concentration (7.8 mg uranyl nitrate in 100 mL water) when aluminum sulfate was added at a rate of 10 mg/L. The simultaneous addition of 2 to 3 mg/L of activated charcoal increased the removal of uranium to about 60%. Essentially complete removal of uranium was achieved by the use of aluminum sulfate alone when the concentration of this flocculant was increased to 40 mg/L (pH not stated). Under laboratory conditions a settling time of one hour was sufficient to achieve effective decontamination. It should be noted that the initial concentration of uranium in these test solutions was 1,000 to 30,000 times greater than that normally encountered in U.S. potable waters, and that the amount of added coagulant varied from about one-half to twice the amounts considered typical for many U.S. municipal water treatment plants (Durfor and Becker, 1964). The conditions under which Weissbuch, Cotrau, and Velicescu performed their experiments are thus not identical to conditions likely to be encountered in typical U.S. water supplies; nevertheless, it appears probable that the normal procedure of many U.S. municipal water treatment plants (i.e., flocculation with alum followed by filtration) removes, or

can be readily modified to remove, some or most of the uranium present in the raw feed water. This observation is at odds with an opinion stated in an early Water Quality Criteria Report (1968) that coagulation, sedimentation, and rapid sand filtration have little effect on the concentration of uranyl ions in surface water; consequently, verification of this conclusion using feed water with more typical uranium concentrations and closer duplication of standard municipal water treatment plant practices are desirable.

Laskorin, Metalnikov, and Terentiev (1960) and Laskorin, Metalnikov, and Smolina (1977) also studied the removal of uranium from natural fresh water. Although their aim was the recovery of uranium rather than the purification of water, in some respects their experimental conditions were more pertinent to our task than were those reported by Weissbuch, Contrau, and Velicescu. For example, Laskorin et al. conducted most of their experiments with natural lake waters (pH 8.4 to 8.7) containing about 60 µg/L uranium, a not unusual concentration in some heavily uranium-contaminated U.S. groundwaters.

Laskorin et al. examined many sorbents and coprecipitants. Calcium phosphate gel, bone crumbs, Sokolovo bauxite, aluminum hydroxide gel, and ferric hydroxide gel were found to adsorb uranium; however, the adsorption capacity of these materials varied greatly. When lake water contained added uranium (total uranium, 200 µg/L), ferric hydroxide gel had the greatest capacity for adsorbed uranium (60.1 mg/mL), but this loading decreased rapidly to only 0.07 mg/mL for lake water containing no added uranium (total uranium, 60 µg/L). For lake water with no added uranium, calcium phosphate gel and aluminum hydroxide gel had the best uranium adsorption capacities, 0.17 and 0.11 mg/mL, respectively. Among synthetic ion exchange resins, cation exchangers were ineffective, because in lake water of pH 8.4 to 8.7, uranium existed mainly as the tricarbonato uranyl anion. However, sorption capacities of 0.18-0.19, 0.24-0.27, and 0.24-0.26 mg/mL uranium were measured for the anion exchange resins, ED-10P, EDE-10, and AH-2F, respectively. Data defining minimum concentrations of uranium in treated water were not provided as the authors were interested in uranium recovery, not water purification.

Among the various methods examined for recovering uranium from lake water, Laskarin and coworkers preferred coprecipitation with aluminum hydroxide, followed by settling, filtration, dehydration, and recovery of the uranium by dissolution in acid. They achieved yields of 80 to 90% using 8 to 24 µg/L aluminum sulfate. Under the conditions of their experiments, adsorption of uranium on the flocculant occurred within a few seconds.

As in the case of Weissbuch and coworkers, the research results reported by Laskorin et al. are not directly transferable to the purification of U.S. drinking waters. Nevertheless, their chemical treatments and process equipment are so similar to those used in typical U.S. water treatment plants (see Appendix 1) that some removal of uranium must be presumed to occur, or can be readily made to occur, in present-day U.S. municipal water treatment plants. Obviously, verification of this presumption should be possible by comparing the uranium content of raw and treated waters from various U.S. water purification plants, taking into consideration the water sources and the treatment methods employed (Table 2). Unfortunately, no firm conclusions are now possible, since operators of municipal water treatmert plants customarily perform uranium analyses only on samples of treated, not raw, water. From Table 2 it can be seen that concentrations of uranium in treated water are generally quite low; however, without knowledge of the initial uranium concentration in the untreated water, decontamination factors cannot be determined. Analyses of the uranium in simultaneously drawn samples of raw, partially treated, and finished waters from typical U.S. water treatment plants are needed for this comparison.

Table 2. Uranium in water from U.S. municipal water treatment plants

State and city	Water source		Water treatment						Uranium concentration (ppb)
	Surface[a]	Ground[b]	Coagulation, alum, iron, salt, or sludge	Activated carbon or silica	Sand or diatomaceous earth filtration	Softening	Chlorination	Fluoridation	Treated water
Alabama									
Birmingham	x		x		x		x		<0.1-0.2
Mobile	x		x		x		x	x	0.1
Montgomery		x				x	x		<0.1
Arizona									
Phoenix	x	x	x	x	x		x		1.4-5.5
Tucson		x					x		1.6-7.3
California									
Fresno		x							0.5
Long Beach	x	x	x		x	x	x		<0.1-8.6
Los Angeles	x	x			x	x	x		4.8
Oakland	x						x		<0.1
Sacramento	x	x	x		x		x		<0.1
San Diego	x		x		x	x	x		6.9
San Francisco	x						x		0.2-0.3
San Jose	x	x			x				0.5
Colorado									
Denver	x		x	x	x		x		0.2-2.8
Connecticut									
Bridgeport	x						x		<0.1
Hartford	x				x		x	x	<0.1
New Haven	x				x		x		0.2
District of Columbia									
Washington	x		x		x		x	x	<0.1
Florida									
Jacksonville		x					x		<0.1
Miami		x			x	x	x	x	0.2
St. Petersburg		x	x		x	x	x		0.1
Tampa	x	x	x		x	x	x		0.4
Georgia									
Atlanta	x		x		x		x		<0.1
Savannah	x	x	x		x		x		<0.1
Hawaii									
Honolulu		x					x		<0.1
Illinois									
Chicago	x		x	x	x		x	x	0.1-0.2
Rockford		x					x		0.6

Table 2 (continued)

State and city	Water source		Water treatment						Uranium concentration (ppb)
	Surface[a]	Ground[b]	Coagulation, alum, iron, salt, or sludge	Activated carbon or silica	Sand or diatomaceous earth filtration	Softening	Chlorination	Fluoridation	Treated water
Indiana									<0.1
Evansville	x		x	x	x		x		<0.1
Fort Wayne	x		x	x	x	x	x	x	0.3
Gary	x		x	x	x		x	x	1.3
Indianapolis	x		x	x	x		x		0.2-0.3
South Bend		x					x		
Iowa									1.9
Des Moines	x	x	x		x	x	x	x	
Kansas									2.4
Kansas City	x		x	x	x		x		<0.1
Topeka	x		x	x	x	x	x	x	0.5
Wichita		x			x	x	x		
Kentucky									0.4
Louisville	x		x	x	x	x	x	x	
Louisiana									<0.1
Baton Rouge		x					x		<0.1
New Orleans	x		x	x	x	x	x		<0.1
Shreveport	x		x		x		x		
Maryland									<0.1
Baltimore	x		x		x		x	x	
Massachusetts									0.1
Boston	x						x		<0.1
Springfield	x				x		x		<0.1
Worcester	x						x		
Michigan									0.1
Detroit	x		x	x	x		x		<0.1
Flint	x		x	x	x	x	x		0.2
Grand Rapids	x			x	x		x	x	
Minnesota									0.1
Minneapolis	x		x	x	x	x	x	x	0.1
St. Paul	x		x		x	x	x	x	
Mississippi									0.1
Jackson	x		x	x	x		x		
Missouri									0.2
Kansas City	x		x	x	x	x	x		0.5
St. Louis	x		x		x	x	x	x	

Table 2 (continued)

State and city	Water source		Water treatment						Uranium concentration (ppb)
	Surface[a]	Ground[b]	Coagulation, alum, iron, salt, or sludge	Activated carbon or silica	Sand or diatomaceous earth filtration	Softening	Chlorination	Fluoridation	Treated water
Nebraska									
Lincoln		x			x		x		5.2
Omaha	x		x	x	x	x	x		2.6
New Jersey									
Jersey City	x						x		0.1
Newark	x						x		0.1-0.2
Paterson	x		x	x	x		x		<0.1-0.2
New Mexico									
Albuquerque		x					x		2.9-9.8
New York									
Albany	x		x		x		x		<0.1
Buffalo	x		x		x		x	x	0.2
New York City	x	x					x		0.2-1.0
Rochester	x		x		x		x	x	<0.1
Syracuse	x						x		0.1
Yonkers	x	x			x		x		0.1-0.3
North Carolina									
Charlotte	x		x	x	x		x	x	0.1
Greensboro	x		x		x		x		0.1
Ohio									
Akron	x		x	x	x		x		0.1
Cincinnati	x		x	x	x		x		<0.1
Cleveland	x			x	x		x	x	0.3
Columbus	x		x	x	x	x	x		<0.1
Dayton		x			x	x	x		<0.1
Toledo	x		x	x	x	x	x	x	0.1
Youngstown	x		x	x	x	x	x		0.1
Oklahoma									
Oklahoma City	x		x	x	x	x	x	x	0.3
Tulsa	x		x		x		x	x	0.2
Oregon									
Portland	x						x		0.2
Pennsylvania									
Erie	x		x		x		x		0.3
Philadelphia	x		x	x	x		x	x	<0.1
Pittsburgh	x		x	x	x	x	x	x	<0.1

Table 2 (continued)

State and city	Water source		Water treatment						Uranium concentration (ppb)
	Surface[a]	Ground[b]	Coagulation, alum, iron, salt, or sludge	Activated carbon or silica	Sand or diatomaceous earth filtration	Softening	Chlorination	Fluoridation	Treated water
Rhode Island									
Providence	x		x		x		x	x	<0.1
Tennessee									
Chattanooga	x				x		x	x	0.5
Memphis		x			x		x		<0.1
Nashville	x		x		x		x	x	<0.1
Texas									
Amarillo		x					x		4.9-7.4
Austin	x		x		x	x	x		<0.1
Corpus Christi	x		x		x	x	x	x	0.9
Dallas	x		x	x	x	x	x		0.2
El Paso	x	x	x	x	x	x	x		0.1-5.4
Fort Worth	x		x		x		x		1.4
Houston	x	x	x	x	x		x		0.1-2.2
Lubbock		x					x		3.0-250
San Antonio		x					x		0.3
Utah									
Salt Lake City	x	x	x		x		x		0.5-2.8
Virginia									
Norfolk	x		x	x	x		x		<0.1
Richmond	x		x	x	x		x	x	0.2
Washington									
Seattle	x						x		0.1
Spokane		x					x		3.7
Tacoma	x	x					x		0.2
Wisconsin									
Madison		x					x	x	0.5
Milwaukee	x		x		x		x	x	<0.1

[a] Surface water sources include rivers, other streams, reservoirs, and lakes or ponds.
[b] Groundwater sources include ordinary and artesian wells and springs.

Source: Adapted from Durfor and Becker, 1964.

6. RECOMMENDATIONS

The literature discusses many techniques of recovering uranium from aqueous solutions, but no papers address the specific problem of removing this pollutant from drinking water. In the few papers that contain useful data, there is evidence that, under favorable conditions, uranium at concentrations likely to be encountered in potable water sources may be removed by several processes that are, or could readily become, part of most municipal water treatment procedures. Some of these processes are adsorption on aluminum or iron coagulants, activated carbon or silica, clays, or the cellular walls of microorganisms that compose the schmutzdecke (see Appendix 1) that coats the sand particles of most sand filters used in municipal water treatment plants.

Whether or not uranium is removed in typical municipal water treatment procedures should be easy to ascertain; one need only compare the concentrations of uranium in simultaneously drawn samples of raw and treated water. Unfortunately, such analytical data for comparable raw and treated water samples could not be found for any U.S. municipal water treatment plant. Apparently because of the expense involved, uranium analyses when performed at all are usually made only on treated water samples.

Although almost all such published analyses show very low uranium concentrations, suggesting that uranium removal does indeed occur, it is not possible to verify this effect without analytical data on comparable raw water samples. Priority should therefore be given to securing and analyzing samples of raw and treated water from typical U.S. water treatment plants. Samples should be collected after each step in the treatment process so that effective decontamination procedures can be identified. Collection and analysis of such samples could be implemented at relatively small incremental cost by the U.S. EPA Office of Radiation Programs, Montgomery, Alabama, which already routinely analyzes uranium in treated water samples from 20 municipal water plants across the United States (Table 3). Alternatively, water from the cities shown in Table 4 could be sampled. The waters from these cities contain the highest recorded concentrations of uranium in municipally treated waters that we encountered in our survey of the literature.

Table 3. Cities from which composite drinking water samples are currently taken for uranium analyses

Location	Total uranium concentration July-December 1977 composite (pCi/L)
Barnwell, South Carolina	0.047
Berkeley, California	0.041
Bismarck, North Dakota	0.123
Chicago, Illinois	0.379
Columbia, South Carolina	0.027
Columbus, Ohio	0.065
Denver, Colorado	2.280
Harrisburg, Pennsylvania	0.030
Knoxville, Tennessee	0.062
Las Vegas, Nevada	5.341
Los Angeles, California	2.933
Lynchburg, Virginia	0.065
Miami, Florida	0.181
Montgomery, Alabama	0.044
Niagara Falls, New York	0.263
Oklahoma City, Oklahoma	0.170
Pittsburgh, Pennsylvania	0.141
Portland, Oregon	0.028
Santa Fe, New Mexico	0.303
Trenton, New Jersey	0.037

Source: U.S. Environmental Protection Agency, 1979.

If the results of the study suggested above are inconsistent or inconclusive, it is recommended that laboratory studies be initiated under controlled conditions to determine if existing municipal water treatment procedures adequately remove, or can be readily modified to adequately remove, uranium from drinking water. The studies should include conventional water plant coagulants and adsorbents, such as alum, iron salts, activated carbon and silica, and schmutzdecke, as well as natural and

Table 4. Municipal plants producing treated water with relatively high concentrations of uranium

Location	µg/L	pCi/L (computed)
Albuquerque, New Mexico	9.80	6.66
Amarillo, Texas	7.40	5.03
Des Moines, Iowa	1.90	1.29
Denver, Colorado	2.80	1.90
El Paso, Texas	5.40	3.67
Fort Worth, Texas	1.40	0.95
Houston, Texas	3.60	2.45
Kansas City, Missouri	2.40	1.63
Lincoln, Nebraska	5.20	3.54
Long Beach, California	8.60	5.85
Los Angeles, California	4.80	3.26
Lubbock, Texas	13.00-250.00	8.84-170.00
Midland, Michigan	20.00	13.60
Omaha, Nebraska	2.60	1.77
Phoenix, Arizona	5.50	3.74
Salt Lake City, Utah	2.80	1.90
San Diego, California	6.90	4.69
Sault St. Marie, Michigan	37.00	25.16
Spokane, Washington	3.70	2.52
Tucson, Arizona	6.20	4.22

Source: Durfor and Becker, 1964; Scott and Barker, 1962; U.S. Environmental Protection Agency, 1979.

synthetic ion exchangers. Adsorption should be studied as a function of uranium concentration in raw water, type and concentration of adsorbent, adsorption pH, adsorption kinetics, and influence of common cationic and anionic impurities. The aim of the research should be the adaptation of existing water treatment practices with minimal economic impact. Studies are also needed to determine the operating conditions for optimum uranium removal by the electrodialysis and reverse osmosis processes. Neither

of these processes is likely to be the method of choice for the removal of uranium from drinking water in communities with a heavy investment in conventional water treatment equipment and access to supplies of good quality fresh water. One of these treatment processes, though, may well be chosen for use by communities without such supplies of water or by communities that must expand service beyond the capacity of such existing supplies. The electrodialysis and reverse osmosis studies should determine uranium removal as a function of membrane type, membrane preparation methods, pH, pressure/voltage, and feed water composition, including turbidity and common cationic and anionic impurities.

Attention should also be directed to the development of appropriate techniques for removing uranium from drinking water that is supplied by sources other than municipal water treatment plants. It is likely that the most serious exposures to uranium-polluted water occur among the small fraction of the population that consumes unprocessed water from private wells located in uraniferous strata. Although relatively few drinking water wells are known to contain high concentrations of uranium, water from some wells contains uranium in excess of 100 ppb and may contain more than 400 ppb (Wagoner, 1979). Since the required volume of treated water from private wells is much smaller (minimum for drinking water, 2 L per person per day) than that from municipal water plants, normal constraints imposed by capital investment requirements for municipal water plants do not apply, and techniques not feasible for municipal water plants can be considered for private wells. Very likely, convenience, rather than operating cost or capital investment, would be the dominant consideration. Under these circumstances, ion exchange chromatography, adsorption on suitable substrates, such as molecular sieves or hydrous metal oxides, or a membrane process such as electrodialysis or reverse osmosis would probably be the preferred purification method. Such a choice would probably allow use of much present-day water softening methodology and equipment. However, loading and extraction efficiency studies would be needed to define the best types of adsorbents, ion exchange resins, or membranes, as well as optimum operating conditions for the removal of uranium from typical U.S. groundwaters. Information of this type is not now available from either commercial water treatment equipment vendors or industrial users of this equipment (Appendix 2).

7. REFERENCES

Astheimer, L., H. J. Schenk, and K. Schwochau. 1978. Recovery of Uranium from Sea Water or Comparable Solutions. Ger. Offen. 781123, Patent No. 2722838.

Barannik, V. P., V. A. Zhorov, S.V.L. Yashenko, A. I. Kirchanova, and A. G. Kobylyanskaya. 1976. Use of Ampholytes for Removing Trace Elements from Sea Water by a Froth Flotation Method. Izv. Vyssh, Uchebn. Zaved. Tsvetn. Metall. 76(5):8-12.

Beverly, R. J. 1980. Union Carbide Corporation, Metals Division, Grand Junction, Colorado. Personal communication to J. S. Drury, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Blane, D. W., and E. L. Murphy. 1976. Removal of Plutonium and Uranium from Wastewater Using Bone Char. Report MLM-2371, Mound Laboratory, Miamisburg, Ohio. 10 pp.

Brits, R.J.N., and M.C.B. Smit. 1977. Determination of Uranium in Natural Water by Preconcentration on Anion-Exchange Resin and Delayed-Neutron Counting. Anal. Chem. 49(1):67-69.

Bruce, F. R., J. M. Fletcher, H. H. Hyman, and J. J. Katz (eds.). 1956. Progress in Nuclear Energy, Series III, Process Chemistry. McGraw-Hill Book Co., Inc., New York. 407 pp.

Bruce, F. R., J. M. Fletcher, and H. H. Hyman (eds.). 1958. Progress in Nuclear Energy, Series III, Process Chemistry, Vol. 2. Pergamon Press, New York. 579 pp.

Bruce, F. R., J. M. Fletcher, and H. H. Hyman (eds.). 1961. Progress in Nuclear Energy, Series III, Process Chemistry, Vol. 3. Pergamon Press, New York. 474 pp.

Buros, O. K. 1979. Economic Aspects of Membrane Processes. Desalination 30:595-603.

Cameron, A. R., and G. Leclair. 1975. Extraction of Uranium from Aqueous Solutions by Coals of Different Rank and Petrographic Composition. Geo. Surv. Can. 75-35. 11 pp.

Chen, A.C.T., L. I. Gordon, M. R. Rodman, and S. E. Binney. 1979. Selected Bibliography for the Extraction of Uranium from Seawater: Evaluation of Uranium Resources and Plant Siting, Vol. 2. Report No. GJBX-35(79), U.S. Department of Energy, Grand Junction Office, Grand Junction, Colorado. 279 pp.

Davies, R. V., J. Kennedy, R. W. McIlroy, and R. Spence. 1964. Extraction of Uranium from Sea Water. Nature 203(4950):1110-1115.

Davis, T. A., J. S. Wu, and B. L. Baker. 1971. Use of the Donnan Equilibrium Principle to Concentrate Uranyl Ions by an Ion-Exchange Membrane Process. Am. Inst. Chem. Eng. J. 17(4):1006-1008.

Dehn, J. 1980. National Enforcement Investigations Center, Denver, Colorado. Personal communication to J. S. Drury, Oak Ridge National Laboratory Oak Ridge, Tennessee.

Deutscher, R. L., and A. W. Mann. 1977. Determination of Uranium in Natural Waters by Differential-Pulse Polarography of a Trioctylphosphine Oxide Extract. Analyst 102:929-933.

Durfor, C. N., and E. Becker. 1964. Public Water Supplies of the 100 Largest Cities in the United States. Geological Survey Water-Supply Paper 1812. U.S. Government Printing Office, Washington, D.C. 364 pp.

Egawa, H., and H. Harada. 1979. Recovery of Uranium from Sea Water by Using Chelating Resins Containing Amidoxime Groups. Nippon Kagaku Kaishi 7:958-959.

Faris, J., and R. F. Buchanan. 1966. Anion Exchange in Nitrate Solutions. In: Progress in Nuclear Energy, Series IX, Analytical Chemistry, Vol. 6, D. C. Stewart and H. A. Elion, eds., Pergamon Press, New York. pp. 149-180.

Freiser, H. 1970. Some Recent Developments in Solvent Extraction. Crit. Rev. Anal. Chem. 1:47-72.

George, D. R., and J. B. Rosenbaum. 1970. Ion Exchange in the Process Industries Conference. Soc. Chem. Ind. (London) Monogr. Vol. 7. pp. 155-161.

Goldstein, A. L. 1979. Electrodialysis on the American Continent. Desalination 30:49-58.

Gorbushina, L. V., L. Ya. Zhil'tsova, E. N. Matveeva, N. A. Surganova, V. G. Tenyaev, and V. G. Tymenskii. 1972. Extraction-Scintillation Method for Determining the Concentration of Radioisotopes. J. Radioanal. Chem. 10(2):165-172.

Harrington, F. E., R. Salmon, W. E. Unger, K. B. Brown, C. F. Coleman, and D. J. Crouse. 1974. Cost Commentary on a Proposed Method for Recovery of Uranium from Sea Water. Report ORNL-TM-4757, Oak Ridge National Laboratory, Oak Ridge, Tennessee. 79 pp.

Hathaway, L. R., and G. W. James. 1975. Use of Chelating Ion-Exchange Resin in the Determination of Uranium in Ground Water by X-Ray Fluorescence. Anal. Chem. 47(12):2035-2037.

Heide, E. A., K. Wagener, M. Paschke, and M. Wald. 1973. Extraction of Uranium from Sea Water by Cultured Algae. Naturwissenschaften 60(9):431.

Heitkamp, D., and K. Wagener. 1977. Recovering Dissolves Heavy Metals from Seawater. Ger. Offen. 780921, Patent No. 2711609.

Higgins, I. 1980. Chemical Separations Corporation, Oak Ridge, Tennessee. Personal communication to J. S. Drury, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Hodge, V. F. 1975. Semi-Quantitative Determination of Uranium, Plutonium, and Americium in Sea Water. Anal. Chem. 47(11):1866-1868.

Hodge, V. F., F. L. Hoffman, R. L. Foreman, and T. R. Folsom. 1974. Simple Recovery of Plutonium, Americium, Uranium, and Polonium from Large Volumes of Ocean Water. Anal. Chem. 46(9):1334-1336.

Horikoshi, T., A. Nakajima, T. Sakaguchi. 1979. Studies on the Accumulation of Heavy Metal Elements in Biological Systems. IX. Uptake of Uranium from Sea Water by *Synechococcus elongatus*. J. Ferment. Technol. 57(3):191-194.

Ito, H., Y. Yamazaki, and Y. Kantake. 1977. Uranium Adsorbents. Japan. Kokai 77114587.

Jilek, R., J. Fuska, and P. Nemec. 1978. Biological Sorbents for the Decontamination of Uranium Waters. Biologia 33(3):201-207.

Jilek, R., H. Prochazka, J. Fuska, P. Nemec, and J. Katzer. 1974. Deactivation Treatment of Mine Waters and Waste Solutions from the Workup of Uranium Ores. Czech. Patent No. 155832.

Jude, E., and N. Fratila. 1974. Recovery of Uranium Compounds in Mine Waters by Ion Flotation. Proc. of 10th Int. Miner. Process. Congr. 74:707-715.

Juenger, E., and E. R. Schmidt. 1974. Extraction of Uranium (IV) from Mixed Aqueous-Organic Solutions of Nitric Acid with Trioctylmethylammonium Nitrate (Aliquat 336). Monatsh. Chem. 105(1):148-155.

Kanno, M. 1977. Extraction of Uranium from Sea-Water. Proc. Conf. on Nuclear Power and Its Fuel Cycle, Salzburg, 2-13 May 1977. Vol. 2, International Atomic Energy Agency, Vienna. pp. 431-443.

Katz, W. E. 1979. The Electrodialysis Reversal (EDR) Process. Desalination 28:31-40.

Keen, N. J. 1977. Recovery of Uranium from Sea Water. Chem. Ind. (London) 77(14):579-582.

Keil, R. 1979. Highly Selective Spectrophotometric Trace Determination of Uranium (VI) by [illegible] Following Purification and Concentration by Extraction. Fre[illegible]hem. 297(5):384-387.

Kennedy, J. F., A. S. Barker, A. W. Nicol, and A. Hawkins. 1973. Poly (4- and 5-acrylamidosalicyclic) acid. IV. Selectivity in the Extraction of Metal Cations from Aqueous Solutions. J. Chem. Soc., Dalton Trans. 73(11):1129-1132.

Khan, S., and M. Saleem. 1973. Bibliography on the Extraction of Uranium from Sea Water. At. Energy Miner. Cent. Pak., (Rep.) No. 126. 45 pp.

Kim, Y. S., and H. Zeitlin. 1971. Separation of Uranium from Seawater by Absorbing Colloid Flotation. Anal. Chem. 43(11):1390-1393.

Konstantinova, M., and S. Mareva. 1977. Effect of Composition of the Aqueous Phase on Synergic Extraction of Uranium (VI) with Trioctylphosphine Oxide and Organic Acid. Dokl. Bolg. Akad. Nauk. 30(9): 1289-1291.

Korkisch, J. 1966. Ion Exchange in Mixed and Non-aqueous Media. In: Progress in Nuclear Energy, Series IX, Analytical Chemistry, Vol. 6, D. C. Stewart and H. A. Elion, eds., Pergamon Press, New York. pp. 1-94.

Koske, P. H. 1979. Uranium Recovery from the Ocean. The Layout of an Industrial Plant with Respect to the Concept of Fluidized Adsorber Beds. Ges. Kernenergieverwert. Schiffbau Schiffahrt, (Ber.) Gkss. 79/E/14; 33 pp.

Koyanaka, Y. 1970. Collection of Uranium from Sea Water by Galena. J. Nucl. Sci. Technol. 7(8):426-427.

Kraus, K. A., and F. Nelson. 1956. Metal Separations by Anion Exchange, Symposium on Ion Exchange and Chromatography in Analytical Chemistry, ASTM Spec. Tech. Pub. No. 195, p. 27.

Kremen, S. S. 1979. Means by Which Reverse Osmosis Desalting Costs Can Be Substantially Reduced Well Before the Year 2000. Desalination 30: 59-68.

Kuleff, I., and K. N. Kostadinov. 1978. Epithermal Neutron-Activation Determination of Uranium in Environmental Waters by Np-239 After Preconcentration on Activated Carbon. J. Radioanal. Chem. 46(2):365-371.

Larson, T. J., and G. Leitner. 1979. Desalting Seawater and Brackish Water: A Cost Update. Desalination 30:525-539.

Laskorin, B. N., S. S. Metalnikov, and A. S. Terentiev. 1961. Extraction of Uranium from Natural Water. In: Progress in Nuclear Energy. Series III, Process Chemistry, Vol. 3, F. R. Bruce, J. M. Fletcher, and H. H. Hyman, eds., Pergamon Press, New York. pp. 42-51.

Laskorin, B. N., S. S. Metalnikov, and G. I. Smolina. 1977. Extraction of Uranium from Natural Waters. (USSR) At. Energy 43(6):472-476. (Russian).

Llewelyn, G.I.W. 1976. Extraction of Uranium from Sea Water. Atom (London) 238:214-219.

Mgren, L. 1980. Technic Central Systems, Inc. Seattle, Washington. Personal communication to J. S. Drury, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Miyazaki, H. 1977. Extraction of Uranium from Sea Water. Development of Adsorbents. Shikoku Kokenkai Ho 28:16-20.

Morrow, R. J. 1970. Ion Exchange and Solvent Extraction. In: Progress in Nuclear Energy, Series IX, Analytical Chemistry, Vol. 10, D. C. Steward and H. A. Elion, eds., Pergamon Press, New York. pp. 183-224.

Mukai, S., and Y. Koyanaka. 1974. Extracting Uranium from Sea Water and Uranium-containing Aqueous Solutions by Galena. Japan. Kokai Tokkyo Koho 740408, Patent No. 74 14443.

Ninomiya, A., K. Sugasaka, and A. Fujii. 1971. Recovery of Metal Ions by Active Carbon-Metal Hydroxide Adsorbents. Kogyo Kagaku Zasshi 74(7):1486-1487.

Novikov, Y. P., and I. M. Lipova. 1976. Uranium Extraction from Sea Water – State of the Art. Izv. Vyssh. Uchebn. Zaved Geol. Razved (Moscow) 1:180-181.

Ogata, N. 1976. Recovery of Uranium from Sea Water. Present Status of the Study and Future Problems. Nippon Kaisui Gakkai-Shi 30(1):3-13.

Ogata, N., and H. Kakihana. 1969. Collection of Uranium in Sea Water. III. Concentration of Uranium in Dilute Solutions with Surface-Active Agents. Nippon Genshiryoku Gakkaishi 11(8):469-476.

Okamoto, S., K. Yamaguchi, and Y. Takahashi. 1979. Japan. Kokai Tokkyo Koho 790404, Patent No. 79 42387.

O'Laughlin, J. W. 1966. Some Neutral Bifunctional Organophosphorus Compounds as Solvent Extracts. In: Progress in Nuclear Energy, Series IX, Analytical Chemistry, Vol. 6, D. C. Stewart and H. A. Elion, eds. Pergamon Press, New York. pp. 95-146.

Ozawa, Y., T. Murata, H. Yamashita, and F. Nakajima. 1979. Uranium Extraction from Sea Water with Composite Hydrous Titanium (IV) - Iron (II) Oxide. J. Nucl. Sci. Technol. 16(9):671-678.

Peppard, D. F. 1961. Applications of Liquid-Liquid Extraction in Inorganic Separations. In: Progress in Nuclear Energy, Series IX, Analytical Chemistry, Vol. 2, C. E. Crouthamel, ed., Pergamon Press, New York. pp. 201-223.

Peppard, D. F., G. W. Mason, A. F. Bollmeier, Jr., and S. Lewey. 1973. Extraction of Uranium from an Aqueous Solution. U.S. Patent No. 3745205.

Pradzynski, A. H., R. E. Henry, and E. L. Draper, Jr. 1976. Determination of ppb Concentrations of Uranium, Thorium, and Molybdenum in Water Using APDC Preconcentration and Radioisotope Excited Energy Dispersive X-Ray Emission Spectrometry. Proc. ERDA Symp. X-, Gamma-Ray Sources Appl. Nucl. React. Lab., Univ. Texas, Austin, Texas. 1976. NTIS, Springfield, Virginia. pp. 175-177.

Putral, A., and K. Schwochau. 1978. Use of Silica Gel in the Separation of Uranium from Sea Water. Fresenius' Z. Anal. Chem. 291(3):210-212.

Rodman, M. R., L. I. Gordon, and A.C.T. Chen. 1979. Extraction of Uranium from Seawater: Evaluation of Uranium Resources and Plant Siting. Report GJBX-35(79)(Vol. I). Corvallis (USA). School of Oceanography, Oregon State University. 163 pp.

Ross, J. R., and D. R. George. 1971. Recovery of Uranium from Natural Mine Waters by Countercurrent Ion Exchange. U.S. Bur. Mines Report RI-7471. 17 pp.

Rouse, J. 1980. Envirologic Systems, Denver, Colorado. Personal communication to J. S. Drury, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Ryabinin, A. I., E. A. Lazareva, and G. A. Doroshenko. 1973. Sorption of Uranium from Black Sea Water by Anion Exchangers. Radiokhimiya 15(3):437-440.

Sakamoto, F., and H. Tani. 1977. Heavy Metal Adsorbing Agent. Japan. Kokai Tokkyo Koho. Patent No. 77 29890.

Sastri, V. S., and A. W. Ashbrook. 1976. Reverse Osmosis Performance of Cellulose Acetate Membranes in the Separation of Uranium from Dilute Solutions. Sep. Sci. 11(4):359-374.

Sato, T., S. Kotani, and M. L. Good. 1974. Extraction of Anionic Actinide Compounds from Aqueous Solutions by Long Chain Ammonium Compounds. III. Uranium (VI) - Thiocyanate System. J. Inorg. Nucl. Chem. 36(2):451-454.

Scott, R. C., and F. B. Barker. 1962. Data on Uranium and Radium in Ground Water in the United States 1954 to 1957. Geological Survey Professional Paper 426. United States Government Printing Office, Washington, D.C. 115 pp.

Shigetomi, Y., T. Kojima, and M. Shinagawa. 1976. Extraction of Uranium (VI) from Sea Water Using Titanium Hydroxide - Polyacrylamide Gel by a Batch Method. Nippon Genshiryoku Gakkaishi 18(12):796-799.

Shigetomi, Y., T. Kojima, and M. Shinagawa. 1976. Concentration of Uranium from Sea Water by Interfacial Electrolysis. Nippon Genshiryoku Gakkaishi 18(7):452-457.

Shumate, S. E., II, G. W. Strandberg, and J. Parrott, Jr. 1979. Biological Removal of Metal Ions from Aqueous Process Streams. Biotechnol. Bioeng. Symp. 8:13-20.

Sorg, T. J., and G. S. Logsdon. 1980. Treatment Technology to Meet the Interim Primary Drinking Water Regulations for Inorganics: Part 5. J. Am. Water Works Assoc. 72(7):411-422.

Spiegler, K. S. 1977. Salt-Water Purification, 2nd ed., Plenum Press, New York. p. 116.

Steele, T. W., and L. Taverner. 1959. A Review of the Chemical Methods for the Determination of Uranium in Ores, Residues, and Products Arising During Processing. In: Progress in Nuclear Energy, Series IX, Analytical Chemistry, Vol. 1, M. T. Kelley, ed., Pergamon Press, New York. pp. 75-103.

Stevenson, C. E., E. A. Mason, and A. T. Gresky (eds.). 1970. Progress in Nuclear Energy, Series III, Process Chemistry, Vol. 4. Pergamon Press, New York. 675 pp.

Tabushi, I., Y. Kobuke, and T. Nishiya. 1979. Extraction of Uranium from Seawater by Polymer-bound Macrocyclic Hexaketone. Nature (London) 280 (5724):665-666.

Takai, N., K. Takase, and T. Yamabe. 1971. Separation of Uranium from Sea Water Using Hydroxylapatite. Seisan-Kenkyu 23(2):76-77.

Taniguchi, H., H. Nakayama, and H. Tani. 1978. Hippuric Acid Formaldehyde Copolymer Adsorbent. Japan Kokai 780315. Patent No. 78 27692.

Taniguchi, H., H. Nakayama, and H. Tani. 1978. Heavy Metal Adsorbents. Japan Kokai 780318. Patent No. 78 29393.

Technology Newsletter. 1980. Japanese Will Step Up Efforts to Recover Uranium from Sea Water. Chem. Week 126:42.

Tsujino, T., T. Aochi, T. Hoshino, T. Murase et al. 1970. Process Study for Aqueous Reprocessing. VIII. Improvement of Decontamination Factor by the Use of Di-n-butyl Phosphate (DBP) Complexes. Tokai Jigyo-sho, Doryoku-do, Kaku-nenryo Kaihatsu Jigyo-dan (Rep.) N831-70-02:77-78.

U.S. Environmental Protection Agency. 1979. Environmental Radiation Data Report 16, Office of Radiation Programs, Montgomery, Alabama. p. 16.

Wagoner, J. L. 1979. Hydrogeochemical and Stream Sediment Reconnaissance Basic Data Report for Williams NTMS Quadrangle, Arizona. Lawrence Livermore Laboratory Report UCRL-52671. GJBX-71(79). 55 pp.

Water Quality Criteria. 1968. Report of the National Technical Advisory Committee to the Secretary of the Interior, Washington, D.C. Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. p. 20.

Weissbuch, H., A. Cotrau, and P. Velicescu. 1969. Removal of Dissolved Radioactive Elements from Water by Treatment with Flocculating Agents. Z. Gesamte Hyg. Ihre Grenzgeb. 15(10):761-763.

Wilhelms, K. E. 1972. Removing Anions from Water or Aqueous Solutions with Brown Coal or Peat. Ger. Offen. 730222, Patent No. 2206445.

Wooten, M. J., C. Hirayama, A. J. Panson, and J. T. Patton. 1976. Uranium Recovery from Seawater. U.S. National Technical Information Service PB-253482. 52 pp.

Yamabe, T., and N. Takai. 1970. Separation of Uranium from Sea Water by Precipitation Method. Nippon Kaisui Gakkai-Shi 24(127):16-19.

Zhorov, V. A., V. P. Barannik, S. V. Lyashenko, A. I. Kirchanova, and A. G. Kobylyanskaya. 1976. Use of Adsorption Colloidal Flotation for Separating Trace Elements of Sea Water. Izv. Vyssh. Uchebn. Zaved Tsvetn. Metall. 76(6):12-16.

Zivanov, Z., D. Miskovic, and E. Karlovic. 1977. Uranium Recovery from Aqueous Solutions by Flotation with Dimethyldistearylammonium Chloride as a Collector. Zb. Prir. Nauke. Matica Srp. 52:239-247.

APPENDIX 1

U.S. Municipal Water Treatment Practices

Public water supplies are subjected to a variety of treatments, depending on the condition of the raw water and the needs of the consuming community. The following discussion is based on the principal steps involved in treating a hypothetical "very hard" surface water that is laden with silt (Durfor and Becker, 1964). Few municipalities will employ all of the indicated processes, but most will utilize several. In most instances groundwaters undergo less extensive processing than surface waters. These processes usually include disinfection, ion exchange, or occasional lime softening. Treatment of surface waters may include some or all of the following processes dependent on water quality. These processes may include screening, coagulation, precipitation, filtration, ion exchange, lime softening, post-chemical treatment, and disinfection. Following are brief descriptions of these processes.

Screening

Water is pumped through grates to remove tree limbs and other floating debris.

Coagulation and precipitation

After screening, coagulation and precipitation chemicals are added to the water to remove sediments, turbidity, color, and organic matter. Coagulation and precipitation processes change the properties of dissolved, colloidal, and suspended materials so that contaminants settle out of solution by gravity. The stability of colloids and suspended or dissolved solids is due to electrical charge and solvation effects. An effective coagulant changes the surface charge properties of particles so that they tend to agglomerate, or it enmeshes particles in a polymeric suspension that readily settles under the influence of gravity. Commonly used coagulants include alum [$Al_2(SO_4)_3 \cdot 14H_2O$], ferric chloride ($FeCl_3$), ferrous sulfate ($FeSO_4$), lime [$Ca(OH)_2$], and a variety of polymers and

clays. An effective precipitant is a chemical that combines with a dissolved contaminant to form an insoluble compound that settles out of solution or can be readily removed by filtration. Typical precipitants include soda ash (Na_2CO_3), caustic soda (NaOH), and potassium permanganate ($KMnO_4$).

Coagulants and precipitants are usually added to raw water in solid, slurry, or dissolved form, with 1 to 2 minutes of rapid mixing, followed by reduced agitation for about 30 minutes to stimulate floc growth. After the flocs reach optimum size, the treated water passes to primary and secondary settling basins where most of the solids separate from the water after a residence time of several hours.

The kind and amounts of coagulants and precipitants added to raw water vary depending on the nature of the influent water. Raw water containing less than 50 mg/L total dissolved or suspended solids is difficult to treat effectively because flocs do not readily form in such a dispersed system. On the other hand, treatment of water containing dissolved or suspended solids in excess of 2000 mg/L is also troublesome because settling of the agglomerated solids is hindered. The pH of the water is important for effective coagulation. When alum is used, the most effective coagulation occurs in the pH range of 5 to 7; with lime, a pH of 7 to 10 is preferred. Following coagulation, some sort of neutralization is usually performed to return the pH of the treated water to a value near 7.

Coagulation and precipitation produce considerable quantities of sludge solids. Typically, alum produces 0.45 kg for each 100 to 200 g of added aluminum. Lime produces about 450 to 600 kg of sludge per 1000 m^3 of soft water, while the use of anhydrous ferric chloride under similar circumstances results in about 50 kg of solids. Such large quantities of sludge present substantial disposal problems. Scaling can also be a problem when large quantities of solids are present.

Filtration

Clarified water from the settling basins is typically filtered through several feet of fine sand or through a layer of anthracite coal (anthrafilt) to remove the remaining suspended matter and most bacteria. After several days of use, a freshly cleaned bed of filter sand develops a slimy deposit of sediment and bacteria, called schmutzdecke, which may remove bacteria from water (Durfor and Becker, 1964) and may be effective in reducing the uranium content of treated water (Shumate, Standberg, and Parrott, 1979). Filters charged with crushed anthrafilt also have a potential for removing uranium (Cameron and Leclair, 1975).

If the treated water was previously softened by the addition of lime or lime soda, it is now saturated with calcium carbonate. To prevent subsequent precipitation of this material in water pipes and other equipment, it is desirable to convert the calcium carbonate to a more soluble salt, such as calcium bicarbonate. This is usually accomplished by adding sulfuric acid or by injecting carbon dioxide gas. In some water treatment plants, this stabilization procedure is performed before the filtration step to prevent clogging of filter beds, but other water treatment plants stabilize the water after filtration.

Softening

The presence of calcium and magnesium salts is chiefly responsible for hardness in water. To soften water, the concentration of calcium and magnesium ions must be reduced or removed. In most municipal water treatment plants, softening is accomplished by adding lime or lime and soda ash to the water. The addition of lime or lime and soda ash converts dissolved calcium and magnesium salts into a sludge of insoluble calcium carbonate and magnesium hydroxide. This sludge gradually settles and carries down suspended sediment, bacteria, and finely divided organic matter, thereby increasing the efficacy of the coagulating chemical. In a few municipal water treatment plants, calcium and magnesium in water are replaced with sodium by means of a cation exchange process utilizing zeolites or synthetic ion exchange resins. This water softening process is very effective, but the resulting water may be aggressive, requiring the addition of inhibitors to reduce the corrosivity.

Taste and odor removal

In a sense each water treatment step contributes to the removal of tastes and odor from the treated water. However, some water treatment plants also aerate water to reduce tastes and odors. Some plants may add activated carbon with coagulation and softening chemicals to adsorb undesirable tastes, odors, and colors from treated water. Eventually, this carbon becomes part of the coagulated floc and settles as sludge. The use of activated carbon in municipal water treatment plants is of special interest to this study since some research (Weissbuch, Cotrau, and Velicescu, 1969) indicates it to be effective in removing uranium from water under certain conditions.

Disinfection

Before distribution and use, the stored finished water is usually freed from disease germs and other harmful microorganisms by treatment with chloride, hypochlorite, or chloramine compounds. In some localities, ozone rather than chlorine is used as a disinfectant.

Prior to the 1970s, sometimes chlorine was added to untreated influent water immediately after the screening step as a means of controlling the growth of plants and microscopic organisms that could impart undesirable tastes and odors to the water. This procedure, called prechlorination, generally is not now recommended for most water because of the high probability of forming toxic and carcinogenic haloforms from naturally occurring trace organic compounds in the feed water.

Postchemical treatment

If the treated water is to be fluoridated, sodium fluoride, sodium silicofluoride, or fluorosilic acid is generally added to the water. This addition is usually performed after the filtration step because fluoride can be removed by lime-softening and alum-coagulation treatments. Lime may also be added after filtration if the pH or hardness of the water is less than desired. After processing, the treated water passes to storage reservoirs to await distribution to customers.

APPENDIX 2

Equipment Vendors and Users Contacted

The vendors or users of commercial water treatment equipment and supplies listed in Table 5 were canvassed during the preparation of this report concerning the possible use of their product or system to reduce uranium in drinking water to the ppb level. Most of those contacted had no data for uranium removal. None of those contacted had relevant experimental data for the performance of their system product at ppb concentrations. In general, economic considerations dictate the recovery of uranium from wastewaters down to the ppm level, but neither economic nor legal incentives presently exist for industry to reduce uranium in effluents to concentrations lower than the ppm level. For example, operators of uranium mines in Colorado, Wyoming, and the Grants Mineral Belt, New Mexico (Kermac Nuclear Fuels Corporation, United Nuclear — Homestake Partners, the Anaconda Company, and Union Carbide Corporation), have National Pollutant Discharge Elimination System permits allowing the discharge of effluents containing 2 (average) or 4 (maximum) mg/L uranium (Beverly, 1980; Dehn, 1980; Rouse, 1980). Consequently, there has thus far been no industrial demand for, or commercial development of, processes that reduce uranium in effluents to the ppb level.

Table 5. Commercial and industrial water treatment equipment vendors and users contacted during this study

Equipment vendor or user	Address	Contact
Anaconda Company, Mineral Resources Group	Denver, Colorado	R. McClincy
Babcock and Wilcox Company, Nuclear Fuel Division	Appollo, Pennsylvania	C. Del Signore
Bruner Corporation	Milwaukee, Wisconsin	T. Christiman
Chemical Separations Corporation	Concord, Tennessee	I. Higgins
Consolidated Edison	New York, New York	R. Van Wyck
Diamond Shamrock Corporation, Functional Polymers Division	Cleveland, Ohio	J. Griggs
Dow Chemical, USA	Midland, Michigan	L. LeFevre
Hach Chemical Company	Loveland, Colorado	S. Whitmore
Freeport Uranium Recovery Company	Uncle Sam, Louisiana	J. Jolly
Ionac Chemical Company	Birmingham, New Jersey	F. McGarvey
Nuclear Fuel Services	Rockville, Maryland	R. Idaker
Nuclear Metals, Incorporated	Concord, Massachusetts	A. Gilman
Oak Ridge National Laboratory	Oak Ridge, Tennessee	G. Strandberg S. Hurt J. Johnson
Osmonics, Incorporated	Hopkins, Minnesota	L. Comb
Rainsoft Water Conditioning Company	Elk Grove Village, Illinois	A. Graham
Rohm and Haas	Philadelphia, Pennsylvania	B. Robbins
Technic Central Systems, Incorporated	Seattle, Washington	L. Mgren
The Lindsay Company	St. Paul, Minnesota	D. Windberg
Union Carbide Corporation, Metals Division	Grand Junction, Colorado	R. J. Beverly
Water Equipment Technologies, Incorporated	Palm Beach, Florida	L. Stenger
Watco R.O.	Las Vegas, Nevada	S. Casey
Zeolite Chemical Company	Clayton, New Jersey	R. Fackler

METHODS OF REMOVING URANIUM FROM DRINKING WATER:
II. PRESENT MUNICIPAL WATER TREATMENT AND POTENTIAL REMOVAL METHODS

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ABSTRACT

Uranium analyses of raw water, intermediate stage, and treated water samples from 20 municipal water treatment plants indicated that the present treatment practices were not effective in removing uranium from raw waters when the influent concentration was in the range of 0.1 to 16 µg/L uranium. Laboratory batch tests revealed that the water softening and coagulant chemicals commonly used were able to remove more than 90% of the dissolved uranium (<100 µg/L) in waters if an optimum pH and dosage were provided. Absorbents, titanium oxide and activated charcoal, were also effective in uranium removal under specific conditions. Strong base anion exchange resin was the most efficient uranium adsorbent, and an anion exchange column is a recommended option for the treatment of private well waters containing uranium at higher than desirable levels.

1. URANIUM REMOVAL BY PRESENT MUNICIPAL WATER TREATMENT PROCESSES

The effectiveness of water treatment processes for the removal of inorganic contaminants (including radionuclides) has been summarized by Sorg and Logsdon (1980). However, very little information is available on the effectiveness of current treatment processes in removing uranium. As part of an interagency agreement between the Office of Drinking Water (ODW), the U.S. Environmental Protection Agency (EPA), and the U.S. Department of Energy (DOE), a study of the efficiency of uranium removal in water processed at municipal treatment plants was conducted. Water from 20 municipal water purification plants representing eight states was studied. The municipal plants sampled were chosen by EPA because noticeably higher concentrations of uranium in previous measurements of treated water had been shown there. The study was designed to determine whether existing water treatment practice can remove uranium to safe levels for drinking waters and to investigate variations or additions to water treatment methods for removing the uranium to safe levels.

1.1 SAMPLE COLLECTION

Collapsible polyethylene one-gallon containers with screw caps and shipping cartons were mailed to the sampling personnel at selected municipal water treatment plants or to the EPA regional staff for collection of the water samples. Each sampler received one set of four containers with cartons for each plant and was instructed to collect a raw water sample, a water sample after the coagulation and/or softening step, if applicable, and a treated (end-product) water sample. An extra container was enclosed to be used at the sampler's discretion for sampling the water during another stage of the treatment process. A form letter was enclosed with each set of containers requesting the date of sampling, the water source, and descriptive remarks or measurements regarding the samples taken. The samples received were stored at room temperature, with the exception of the raw water samples which were kept in the refrigerator (4°C).

1.2 SAMPLE ANALYSIS

A raw water sample, a water sample from intermediate stages, and a final treated water sample were analyzed for uranium by neutron activation analysis after concentration of the uranium from the sample solution onto an anion exchange column. The experimental method was similar to that used by Brits and Smit (1977). Optimum conditions for adsorption of the uranium from ammonium carbonate systems with methanol were previously determined by Haggag and Stokely (1981). They reported that greater than 99% of the uranium was adsorbed on the column and that quantities of uranium from 0.01 to 6.6 mg (in 100-mL solution) were retained by the column from a 0.1-*M* ammonium carbonate-methanol system. The efficiency of the method was determined with ^{237}U, a gamma emitter. Controls of deionized water were run at intervals to ensure that the equipment remained free of contamination. Detailed procedures for sample preparation and uranium analysis are presented in the appendix.

1.3 RESULTS AND DISCUSSION

The results show that very little uranium is removed by present water treatment methods. Table 1 summarizes the results of the uranium analyses of the raw water, intermediate stage, and treated water samples and describes the point in the treatment process at which each sample was collected. Uranium concentrations are reported in micrograms per liter (µg/L), and their range is from the minimum detectable concentration (0.01 µg/L) to 17 µg/L. Measurements of pH are also recorded in Table 1. The lowest pH reported was 7.4, and the highest was 9.5. In some instances, the uranium level in the treated water was higher than that in the raw water sample. This probably resulted from blending waters from two different sources, one with a higher uranium level than the other. Most of the plants used a combination of conventional methods — coagulation (alum, lime, iron salts, or polymers), sedimentation, filtration, and chlorination. Very few of the plants employed activated carbon for taste and odor control.

An interesting case in which the uranium analyses suggested that some removal of uranium may have taken place was in the samples from Kansas City,

Table 1. Uranium concentrations in raw water, intermediate stage, and product water samples taken from selected municipal water plants

Location plant	Stage	Date[a]	Source/Description	Analyses	
				pH[b]	U, µg/L[c]
Midland, Mich.	Raw	12-4-80	1 Lake Huron, before Cl_2 added	7.7	0.27 ± 0.03, n = 3
			2 After Cl_2 added	8.0	0.47
	Intermediate		After $Fe_2(SO_4)_3$ coagulation before sand filtration	8.1(7.9)	0.59
	Final			7.8	0.35
Houston, Texas	Raw	11-20-80	San Jacinto River, taken from holding pond	7.4	0.32 ± 0.14, n = 3
	Intermediate		1 After alum coagulation	7.6	0.37
			2 Supernatant after lime stabilization	7.9	0.28
	Final			7.7(7.0)	0.28
Kansas City, Mo.	Raw	12-18-80	Missouri River	8.1(7.9)	5.33 ± 0.23, n = 3
	Intermediate		1 After addition of lime plus Cat-Floc C polymer	8.0(8.6)	4.86
			2 After addition of $Fe_2(SO_4)_3$, Cl_2, NH_3, and $Ca(OH)_2$	9.4(9.9)	4.73
	Final		After sand filtration, Cl_2 disinfection	9.5(9.9)	4.07 ± 0.30, n = 4
Lincoln, Neb.	Raw	12-16-80	Well water	8.0(7.4)	7.29 ± 0.47, n = 3
	Intermediate		1 Filter influent, Cl_2, NH_3, and H_2SiF_6 added	8.3	9.11
			2 Filter effluent	8.4	8.91
	Final		Pump discharge	8.0	7.39
Denver, Colo. — Marston	Raw	1-14-81	1 Blue River & So. Platte River, at prechlorination	7.6	1.60, 1.60
			2	7.6	1.50
	Intermediate		After polymer coagulation plus alum	7.8	1.50
	Final		After filtration	7.8	1.50

Table 1 (continued)

Location plant	Stage	Date[a]	Source/Description	Analyses	
				pH[b]	U, µg/L[c]
Moffat	Raw	2-5-81	Winter Park Ralston Reservoir	7.5(7.5)	15.9 ± 1.58
	Intermediate		1 After alum and iron polymer coagulation	7.2	3.90
			2 After lime addition	7.8(8.3)	4.90
	Final			7.6(7.3)	4.00
San Diego, Calif. — Escondido Vista	Raw	12-26-80	1 Local water (75%)	7.8(7.9)	5.43, 5.10
			2-Calif. aqueduct (25%)	8.1(7.7)	8.15 ± 0.39, n = 3
	Intermediate (blend)		After coagulation with alum and cationic polymer	7.7	6.53
	Final (blend)		After filtration	7.7(7.6)	6.25, 5.60
Alvarado	Raw	12-26-80	San Vicente and El Capitan reservoirs	7.8(7.7)	1.68, 1.90
	Intermediate		After coagulation with $FeCl_3$, lime, CaO	8.2(8.2)	2.12
	Final		After Cl_2 disinfection	8.2(8.2)	2.31, 1.80
Otay	Raw	12-26-80	Barrett Reservoir	7.9(8.0)	1.05, 1.00
	Intermediate		After coagulation with $FeCl_3$	7.7	1.22
	Final		After filtration and Cl_2 disinfection	8.2(8.2)	2.10, 2.30
Sweetwater	Raw	12-26-80	Sweetwater Lake	8.0(8.1)	4.07, 3.30
	Intermediate		Filter influent after coagulation with cationic polymer	8.0(7.7)	4.25
	Final		After filtration and Cl_2 disinfection	8.1(7.8)	3.30
Los Angeles, Calif. — Hawthorne	Raw	12-11-80	Well water plus Cl_2	7.7(8.0)	0.14, 0.29, $\leq$0.10
	Intermediate		1 After lime addition, before sedimentation	8.0	0.43
			2 After sedimentation	7.9	0.30
	Final		After filtration	8.2	0.10, $\leq$0.10

Table 1 (continued)

Location plant	Stage	Date[a]	Source/Description	Analyses	
				pH[b]	U, µg/L[a]
Jensen — Metropolitan Water District	Raw	2-9-81	State project water	7.8	0.30, 0.27
	Intermediate		1 Settled water after alum coagulation	8.0	0.25
			2 Clarified water after filtration	8.2	0.27
	Final			8.2	0.28
Long Beach	Raw	12-9-80	Well water	8.2	0.32
	Intermediate		1 After lime coagulation plus Cl_2	8.1	0.65
			2 After filtration	8.2(7.7)	0.51
	Final		After blending with treated surface water	8.3(7.6)	1.59 ± 0.33, n = 3
Weymouth — Metropolitan Water District	Raw	12-4-80	Colorado River	8.0	6.61, 6.10
	Intermediate		1 Flocculator effluent	8.0	7.51
			2 Sedimentation basin outlet	7.9	7.40
	Final			8.0	6.06, 6.60
Phoenix, Ariz. — Val Vista	Raw	12-10-80	Verde River	8.4	4.45, 4.30
	Intermediate		1 After coagulation with alum	8.1	4.76
			2 Presedimentation before chemical addition	8.4	4.50
	Final		After filtration and chlorination, activated carbon (dual media)	8.2	4.05
Verde	Raw	12-10-80	Verde River	8.3	4.30, 4.10
	Intermediate		1 After coagulation with alum	8.2	4.20
			2 Filter influent	8.2	4.32
	Final		After rapid sand filtration and chlorination, activated carbon	8.2	4.20
Squaw Peak	Raw	1-20-81	Salt River	8.2	1.70
	Intermediate		1 From sedimentation basin after coagulation with alum	7.9	1.40
			2 Effluent from storage	8.2	1.50
	Final		After sand filtration, Cl_2, activated carbon	8.2	1.80

Table 1 (continued)

Location plant	Stage	Date[a]	Source/Description	Analyses	
				pH[b]	U, µg/L[c]
Salt Lake City, Utah City Creek	Raw	2-25-81	City Creek	7.9	1.00, 0.80
	Intermediate		1 Collected at end of flocculation basin		1.00, 1.00
			2 Collected at end of sedimentation basin		0.90, 0.90
	Final				0.90, 1.00
Little Cottonwood	Raw (blend)	3-3-81	Little Cottonwood Creek (22%) Deer Creek Reservoir (78%)	7.9	1.70
	Intermediate		1 After coagulation with alum		1.50, 1.50
			2 After sedimentation		1.30, 1.60
	Final				0.90, 1.00
Big Cottonwood	Raw	2-24-81	Big Cottonwood Creek	8.3(8.1)	0.90
	Intermediate		1 Collected at end of flocculation basin	8.0	0.80
			2 Collected at end of sedimentation basin	8.0	0.80
	Final			8.1	0.80

[a] Date of sampling.

[b] pH recorded at time of analysis; pH reported by water sampler in parentheses.

[c] For replicate analyses (n) greater than 2, values are mean ± 1 standard deviation.

Missouri. The raw water was high in carbonate content (Table 2) as were most of the waters with significant levels of uranium. But, unlike the other water samples, the Kansas City water underwent the highest adjustment in pH during treatment, from 8.1 to 9.5. This information pointed to further investigation of the effects that raising the pH has on the

Table 2. Alkalinity versus uranium content of the municipal water

Sample		pH[a]	$CaCO_3$[b] mg/L	U µg/L
Midland, Mich.		8.0	82	0.27 ± 0.03, n = 3
Houston, Texas		7.0	26	0.32 ± 0.14, n = 3
Kansas City, Mo.	— Raw	8.0(7.9)	172(193)	5.33 ± 0.23, n = 3
	Intermediate 1	(8.6)		4.86
	2	(9.9)	(110)	4.73
	Final	(9.9)	(100)	4.07 ± 0.30, n = 4
Lincoln, Neb.		8.0(7.4)	153(155)	7.29 ± 0.47, n = 3
San Diego, Calif.				
Alvarado	— Raw	7.6(7.7)	100(97)	1.68, 1.90
	Intermediate	(8.2)	(101)	2.12
	Final	(8.2)	(103)	2.31, 1.80
Escondido Vista (Calif. aqueduct)	— Raw	8.0	102	8.15 ± 0.39, n = 3
	Intermediate		(115)	6.53
	Final	(7.6)	(118)	6.25, 5.60
Otay	— Raw	7.9(8.0)	110(122)	1.05, 1.00
	Intermediate			1.22
	Final	(8.2)	(121)	2.10, 2.30
Sweetwater	— Raw	8.0(8.1)	135(120)	4.07, 3.30
	Intermediate	(7.7)	(120)	4.25
	Final	(7.8)	(120)	3.30
Los Angeles, Calif.				
Hawthorne		7.9	272	0.14, 0.29, ≤0.10
Jensen				0.30, 0.27
Long Beach	— Raw	8.0	146(134)	0.32
	Final		119	1.59 ± 0.33, n = 3
Weymouth		8.1	114	6.61, 6.10
Denver, Colo.				
Marston		7.5	48	1.60, 1.60
Moffat	— Raw	7.5	29	15.9 ± 1.58
	Intermediate 1	7.2	20	3.90
	2	7.8	32	4.90
	Final	7.6	28	4.00
Salt Lake City, Utah				
Big Cottonwood		(8.1)	(130)	0.90
Little Cottonwood		(7.9)	(136)	1.70
City Creek		(7.9)	(198)	1.00, 0.80
Phoenix, Ariz.				
Val Vista		8.5	218	4.45, 4.30
Verde		8.4	206	4.30, 4.10
Squaw Peak		8.0	115	1.70

[a] pH recorded at time of analysis; pH reported by sampler in parentheses.

[b] Alkalinity reported by sampler in parentheses.

uranium levels in the sample water. Several samples were selected which contained significant levels of uranium such that important losses could be detected (Table 3). Four 100-mL aliquots of sample were placed in separate glass containers and the pH in each was adjusted to 10.0, 10.5, 11.0, and 11.5, respectively, with sodium hydroxide. Depending on the sample, as the pH was raised, a white precipitate appeared in the solution and collected on the bottom of the container. After a few minutes, the sample solution was filtered (0.22-μm pore size) and then analyzed by first preconcentrating the uranium in the solution onto anion exchange resin, followed by neutron activation analysis of the resin. The results given in Table 3 show that by raising the pH of the water, the uranium level may be decreased, with the amount of decrease depending on the sample.

Uranium removal was more accentuated in the sequence of samples taken from the Moffat Plant in Denver, Colorado. The average uranium level for the raw water sample was 15.9 μg/L. However, the uranium level in the postcoagulation sample was only 3.9 μg/L, a 75% decrease from the raw water value. The pH of the raw water sample was 7.5, while the pH of the intermediate sample was 7.2. Alkalinity was in the 20 to 30 mg/L range (Table 2). At the point where the first intermediate sample was taken, the raw water had been treated with aluminum sulfate, but no lime had been added. To determine if the alum coagulation was actually responsible for the uranium removal, an amount of alum equal to 10 mg/L was added to a 100-mL aliquot of the raw water sample, and the solution was allowed to equilibrate with stirring for 20 minutes. Upon addition of the alum, the pH decreased to 7. Then the solution was filtered (0.45-μm pore size), and after additions of ammonium carbonate and methanol, it was passed through an anion exchange column. Neutron activation analysis of the resin showed 3.6 μg/L uranium, a 77% decrease from the uranium level in the raw water.

The Kansas City and Denver (Moffat) results represent opposite effects. For Kansas City, the loss of uranium, although slight, was related to the loss of carbonate (about 50%, Table 2) during softening. The Denver result was a consequence of a low alkalinity, low pH sample (this water is a mixture of softer water from the mountains and harder

Table 3. Effect of raising the pH followed by filtration (0.22 μm) on the uranium concentration in water from U.S. municipal treatment plants

Location	Treatment stage	pH	U, μg/L
Kansas City, Mo.	Intermediate 1	8.0	4.86[a]
		10.0	5.20
		10.5	5.00
		11.0	2.60
		11.5	2.10
San Diego, Calif. Escondido Vista	Intermediate	7.7	6.53[a]
		10.0	5.20
		10.5	2.40
		11.0	1.40
		11.5	0.80
Phoenix, Ariz.	Intermediate 2	8.2	4.32[a]
		10.0	3.80
		10.5	1.20
		11.0	0.36
		11.5	0.38
Lincoln, Neb.	Intermediate 2	8.4	8.91[a]
		12.0	2.80
Long Beach, Calif. Weymouth	Intermediate 1	8.0	7.51[a]
		11.0	1.40
		12.0	2.10

[a]Data from Table 1.

water from a small reservoir receiving uranium from a mining operation) being exposed to the aluminum hydroxide. The uranium was present in an "unstable" state because of blending and probably would have been slowly lost during storage even if treatment had not occurred. Thus this was an exception to the normal stability of uranium during treatment.

2. EXAMINATION OF AVAILABLE REMOVAL METHODS

Numerous studies have been conducted concerning the recovery of uranium from water under special circumstances, but none of the studies attempted concerned the removal of uranium from drinking water through existing municipal water treatment processes (see Part I of this document). Several methods developed for uranium analysis and decontamination processes (Hodge, 1975; Weissbuch, Cotrau, and Veliescu, 1969) could readily become part of a water treatment procedure, but the methods should be tested and optimized because the chemical conditions and objectives of the methods are drastically different from those of municipal water treatment systems.

The objectives of this part of the studies were to evaluate

1. water softeners [$Ca(OH)_2$, $MgCO_3$] as coprecipitators for uranium,
2. coagulants [$Fe_2(SO_4)_3$, $FeSO_4$, $Al_2(SO_4)_3$] as coprecipitators for uranium,
3. adsorbents (TiO_2, activated charcoal) for uranium removal, and
4. ion exchange columns for uranium removal.

Interpretations of the results, particularly for the lime-softening and coagulant experiments, are focused on the effectiveness of the chemicals and optimum conditions for uranium removal. The optimum conditions of the chemical treatments may or may not coincide with the optimum conditions for the lime-softening and coagulation processes applied by water treatment plants. The practicality of the results should, therefore, be examined by laboratory jar tests and pilot plant tests of waters from different sources.

The water used in these studies was taken from Pond 3513, the former final low-level radioactive waste settling basin of the Oak Ridge National Laboratory. After its retirement as a waste effluent settling basin, the pond water was subjected to a rapid turnover by rainwater runoff. We selected this water because the uranium concentration was relatively higher than that of any other natural bodies of water in this region. Analytical data of the water are given in Table 4. The composition, other than radionuclides, of the water is not greatly different from that of the surface water in this area (ORNL-2557, 1959). The pH and concentration of carbonate and other ligand species in the pond water

Table 4. Chemical composition of pond (3513) water[a]

Constituent	Concentration (mg/L)
Total alkalinity (as $CaCO_3$)	100.5
Ca	21.4
Mg	12.9
U	0.08
K	1.9
Na	7.0
SiO_2	2.7
NO_3	0.06
SO_4	14.1
Cl	7.8
PO_4 (inorganic)	0.02
Dissolved oxygen	12.5
pH	8.9

[a]Average concentration from January to July, 1980.

suggest that the dominant uranium in the water would be uranyl carbonates [$UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$] (Langmuir, 1978). Such uranyl carbonate species are expected to be common in most alkaline surface and well waters used as raw water by municipal water treatment plants. The pond water was collected through a filter into 25-L, polyethylene plastic jars using a submerged water pump. The collected water was passed through Whatman No. 42 filter paper to remove fine suspended particulates. Synthetic waters containing various amounts of uranium and other elements were also used in part of the experiments.

Because ^{238}U, an alpha emitter, can be difficult and time consuming to determine, ^{237}U, a gamma emitter, was used to measure the effectiveness of each treatment in removal of uranium. The solution to be used in each experiment was spiked with ^{237}U and equilibrated overnight so that the ^{237}U would have the same chemical form as the natural uranium in the

water. Two aliquots of the solution, removed before the treatment tests, were used as standards for the experiment. A portion of the solution was removed before the spiking for a background (Bkgd) count. The ^{237}U was measured by a Packard Auto-Gamma System incorporating a dual thallium-activated NaI scintillation crystal/dual photomultiplier tube detection system. The counting error, expressed as $100\frac{\sqrt{N}}{N}$, where N is the total number of counts, was always less than 5%. Because the ^{237}U has such a short half-life ($t^{1/2}$ = 6.75 d), error introduced by lags in the counting time for a set of samples was minimized by counting a standard before and after testing each set of samples and using the average counts for calculation of uranium removal. The following relationship was used to determine uranium removal.

$$\% \ ^{237}U \text{ removed} = \frac{(\text{Standard count} - \text{Bkgd}) - (\text{Sample count} - \text{Bkgd})}{(\text{Standard count} - \text{Bkgd})} \times 100$$

2.1 URANIUM REMOVAL BY ALKALINE EARTH WATER SOFTENERS

Lime and lime-soda softening have been a standard practice to remove calcium and magnesium salts, which are the main source of hardness in water. The softening process produces a sludge composed of calcium and magnesium hydroxide. Magnesium carbonate treatment, in addition to lime treatment, was introduced to improve coagulation as well as to recycle the lime and magnesium carbonate (Thompson, Singley, and Black, 1972). Under proper conditions, removal of Ba, Ra, and other trace heavy metals during water-softening processes has also been obtained (Sorg, Csanady, and Logsdon, 1978; Sorg and Logsdon, 1980). Removal of uranium from seawater by sodium hydroxide treatments was observed (Hodge, 1975), but the removal process was not well understood.

2.1.1 Lime [$Ca(OH)_2$] Treatment

Aliquots (200 mL) of ^{237}U-spiked pond water were treated with varying amounts of analytical grade $Ca(OH)_2$. The lime dosages applied in this experiment were near the range of dosages routinely used by municipal plants. About 85 to 90% of the uranium in the pond water was removed by the lime treatments (Table 5). The final pH of the water was

Table 5. Removal of uranium from pond water by $Ca(OH)_2$ treatment[a]

	$Ca(OH)_2$ dose (mg/L)				
	50	100	150	200	250
% U removed	86	85	87	87	90
Final pH	10.6	11.1	11.3	11.5	11.5

[a]Initial U concentration: 83 µg/L.

between 10.6 and 11.5. The pH of the water depended on the lime dosage, but the differences in uranium removal were minimal. Since the efficiency (85–90%) could depend on the total alkalinity, it is difficult to conclude whether the lime treatment is sufficient to remove uranium for all municipal water treatment plants. The concentration of indigenous uranium in the pond water was 0.083 mg/L, and the uranium concentration in the treated water was expected to be 0.008 mg/L, which is probably higher than in many raw waters used by municipal treatment plants.

2.1.2 $Ca(OH)_2$ and $MgCO_3$ Treatment

To investigate the role of $MgCO_3$ addition to a $Ca(OH)_2$ softening system on uranium removal, varying amounts of $MgCO_3$ and $Ca(OH)_2$ powder were added to 200-mL portions of the ^{237}U-spiked pond water. The final pH of each batch was measured after a 20-min stirring period, and the ^{237}U activity remaining in the solution was measured after filtration with 0.45-mm-pore filter.

The $Ca(OH)_2$ and $MgCO_3$ treatment results (Table 6) indicate that:

(1) At a lower dose of $Ca(OH)_2$ (50 mg/L), the $MgCO_3$ additions reduced the effectiveness of $Ca(OH)_2$ for uranium removal (compare with Table 5).

(2) At a $Ca(OH)_2$ dosage higher than 100 mg/L, the percent of uranium removal increased with increase in $MgCO_3$ dose.

(3) At a given $MgCO_3$ dose, the increase of $Ca(OH)_2$ dose from 100 to 250 mg/L did not influence the efficiency of uranium removal.

Table 6. Removal of uranium from pond water by combined $Ca(OH)_2$ and $MgCO_3$ treatment[a]

$MgCO_3$ dose (mg/L)		$Ca(OH)_2$ dose (mg/L)				
		50	100	150	200	250
10	% U removed	32	90	90	88	89
	Final pH	10.6	11.0	11.1	11.3	11.3
40	% U removed	9.0	95	95	94	94
	Final pH	9.8	10.9	10.8	11.1	11.4
80	% U removed	24	98	93	98	98
	Final pH	10.3	10.8	10.7	10.9	11.2
120	% U removed	15	99	99	99	99
	Final pH	9.9	10.6	10.8	11.0	11.2

[a]Initial U concentration: 83 µg/L.

(4) The volume of floc in solution appeared to increase with increasing dosage of $MgCO_3$ and $Ca(OH)_2$.

(5) The critical pH in the $MgCO_3$–$Ca(OH)_2$ system appeared to be near 10.6. Above pH 10.6, with sufficient dosage of $MgCO_3$ and $Ca(OH)_2$, more than 98% of the uranium was removed by the floc.

(6) The optimum dosages of $MgCO_3$ and $Ca(OH)_2$ to remove uranium from the pond water would be 120 and 150 mg/L, respectively.

The dependency of the uranium removal on $MgCO_3$ and $Ca(OH)_2$ dosage added to the pond water suggested that water composition, particularly indigenous Mg, Ca, and carbonate concentration, would be a factor determining the optimum dosage of the treatment chemicals.

2.1.3 pH and Uranium Concentration Effects

To investigate the effect of pH on uranium removal, solutions containing 100 mg/L $Ca(OH)_2$ or 50 mg/L $MgCO_3$ were prepared from the ^{237}U-spiked pond water, and then the pH of the solutions was adjusted to 9, 10, 11, and 12 with HCl and NaOH solutions. For both $Ca(OH)_2$ and $MgCO_3$ solutions, the highest uranium removal was obtained at pH 11, and the uranium removal was reduced at pH 12 in both solutions (Table 7). The

Table 7. Effect of pH at a given $Ca(OH)_2$ and $MgCO_3$ dose on uranium removal from pond water[a]

Adjusted pH	% U removed	
	$Ca(OH)_2$ 100 mg/L	$MgCO_3$ 50 mg/L
9	24	0
10	68	0
11	80[b]	59
12	48	30

[a]Initial U concentration: 83 µg/L.

[b]Compare with Table 5.

$Ca(OH)_2$ solution had a higher removal of uranium than the $MgCO_3$ solution at the given pHs.

In order to study the effects of variations in the indigenous uranium concentration on the efficiency of uranium removal by $Ca(OH)_2$ and $MgCO_3$ treatments, varying amounts of ^{238}U were added to 200-mL aliquots of a 40-mg/L $MgCO_3$ solution which had been spiked with ^{237}U. The batches were allowed to equilibrate overnight. After equilibration, 0.02 g of $Ca(OH)_2$ were added to each 200-mL batch, and the pH was measured. If it was necessary to raise the pH to 10.9, NaOH was used. At this pH and dosage of $MgCO_3$ and $Ca(OH)_2$, previous results (Table 6) had shown >90% uranium removal from the pond water. After a 20-min stirring period, each solution was filtered (0.45-µm pore size) and the ^{237}U measured.

The results shown in Table 8 indicate that at uranium levels of 2.4 µg/L or less, the efficiency of uranium removal is still 90% or better. However, at uranium levels greater than 2.4 µg/L, the efficiency of uranium removal decreases drastically. Section 1 of this report demonstrates that some municipal treatment plants may process raw water with uranium levels which fall in the 0.24- to 24-µg/L range. In these cases, treatment modifications, such as higher dosage of $MgCO_3$ and $Ca(OH)_2$ (Table 6), may be necessary to maximize the efficiency of the uranium removal.

Table 8. Efficiency of uranium removal by $Ca(OH)_2$ and $MgCO_3$ treatment at varying uranium concentrations[a]

	Uranium concentration (µg/L)					
	2.4×10^{-3}	2.4×10^{-2}	2.4×10^{-1}	2.38	23.8	238
% U removed	97	97	93	90	58	54

[a]Dosage: 40 mg/L $MgCO_3$ and 100 mg/L $Ca(OH)_2$.

2.1.4 Discussion

By the addition of $Ca(OH)_2$ to the pond water, most of the CO_2 and bicarbonate alkalinity is converted to calcium carbonate. These well-known stoichiometric reactions are:

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3(s) + H_2O \quad (1)$$

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2\,CaCO_3(s) + H_2O \quad (2)$$

Magnesium bicarbonate in the water is also converted to magnesium carbonate and then to magnesium hydroxide on further addition of $Ca(OH)_2$ as shown by:

$$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow MgCO_3 + CaCO_3(s) + H_2O \quad (3)$$

$$MgCO_3 + Ca(OH)_2 \rightarrow Mg(OH)_2(s) + CaCO_3(s) \quad (4)$$

The addition of $MgCO_3$ to the system requires a higher dosage of $Ca(OH)_2$ to remove the carbonate as $CaCO_3$ and to form magnesium hydroxide, but such additions increase the volume of the flocs composed of $Mg(OH)_2$ and $CaCO_3$. The gelatinous $Mg(OH)_2$ floc acts as a coagulant and thus improves flocculation of the suspended materials (Thompson, Singley, and Black, 1972). Based on the jar test results, Thompson, Singley, and Black (1972) found that good floc formation took place at a pH above 11.0.

Equations 1 through 4 suggest that as the $Ca(OH)_2$ dose increases, the CO_2 and carbonates in the water become depleted and could change the chemical state of the uranium species. The uranium in the pond water is

expected to be present as uranyl tricarbonate, $UO_2(CO_3)_3^{4-}$. The $UO_2(CO_3)_3^{4-}$, known as a relatively stable complex, could be converted to uranyl hydroxide in the carbonate-depleted environment by addition of $Ca(OH)_2$. Ideally, the reaction would be:

$$3\ UO_2(CO_3)_3^{4-} + 9\ Ca(OH)_2 \rightarrow (UO_2)_3(OH)_5^{+} + 9\ CaCO_3(s) + 13\ OH^- \quad . \qquad (5)$$

In the $MgCO_3$–$Ca(OH)_2$ system, the chemical reactions could be:

$$3\ UO_2(CO_3)_3^{4-} + 10\ Ca(OH)_2 + MgCO_3 \rightarrow (UO_2)_3(OH)_5^{+} + Mg(OH)_2(s) + 10\ CaCO_3(s) + 13OH^- \quad . \qquad (6)$$

Such conversion from carbonate to hydroxide was not experimentally proved but is expected to be controlled by the ratio of the free CO_3^{2-} and OH^- in the water. Nevertheless, the two uranyl species are drastically different not only in terms of ligands but also in charge and molecular size of the species. As a result, adsorption or precipitation behavior of the uranyl species is expected to be different.

To answer a part of the questions regarding uranium removal mechanisms, the following experiments were conducted with distilled-demineralized water instead of the pond water.

(1) Magnesium solution: 0.005 *M* $MgCl_2$, 0.05 *M* NaCl, 48 µg/L ^{238}U, and trace ^{237}U spike.

(2) Magnesium bicarbonate solution: 0.005 *M* $MgCl_2$, 0.005 *M* $NaHCO_3$, 0.05 *M* NaCl, 48 µg/L ^{238}U, and trace ^{237}U spike.

(3) Calcium solution: 0.005 *M* $CaCl_2$, 0.05 *M* NaCl, 48 µg/L ^{238}U, and trace ^{237}U spike.

(4) Calcium bicarbonate solution: 0.005 *M* $CaCl_2$, 0.005 *M* $NaHCO_3$, 0.05 *M* NaCl, 48 µg/L ^{238}U, and trace ^{237}U spike.

Two-hundred milliliters of each stock solution was transferred into a 250-mL bottle and NaOH added. The experimental results of the magnesium and magnesium bicarbonate solutions are plotted as percent removal of uranium versus pH and versus volume of 1 *M* NaOH added to the batches (Figs. 1 and 2).

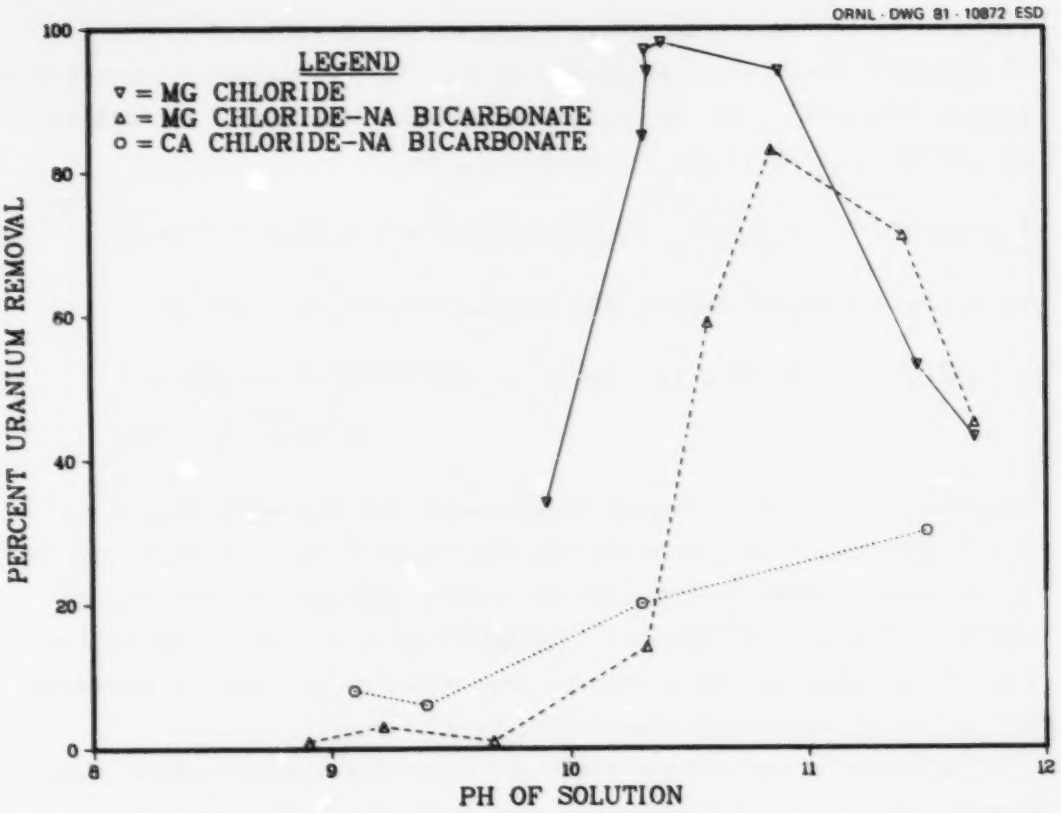

Fig. 1. Percent uranium (initial uranium concentration, 48 μg/L) removed from 5×10^{-3} *M* $MgCl_2$ 5×10^{-3} *M* $MgCl_2$–5×10^{-3} *M* $NaHCO_3$, and 5×10^{-3} *M* $CaCl_2$–5×10^{-3} *M* $NaHCO_3$ solutions at varying pHs.

More than 90% of the uranium in the magnesium solution was removed between pH 10.3 and 10.9 or by an addition of 0.2 to 2.0 mL of 1 *M* NaOH to the 200-mL magnesium solution. In the magnesium-bicarbonate solution, the highest uranium removal was 83% at pH 10.9 with an addition of 2 mL of 1 *M* NaOH. The magnesium-bicarbonate solution consumed more NaOH and required a higher pH than the magnesium solution to remove uranium. In both solutions, the excessive NaOH or a pH higher than 11.4 reduced the efficiency of uranium removal. A separate batch which had 0.1 *M* magnesium and bicarbonate was prepared to examine the role of hydromagnesite [$Mg_4(CO_3)_3(OH)_2 \cdot 3\ H_2O$] precipitate on uranium removal. At an adjusted pH of 9.5, the uranium removal was only 13%.

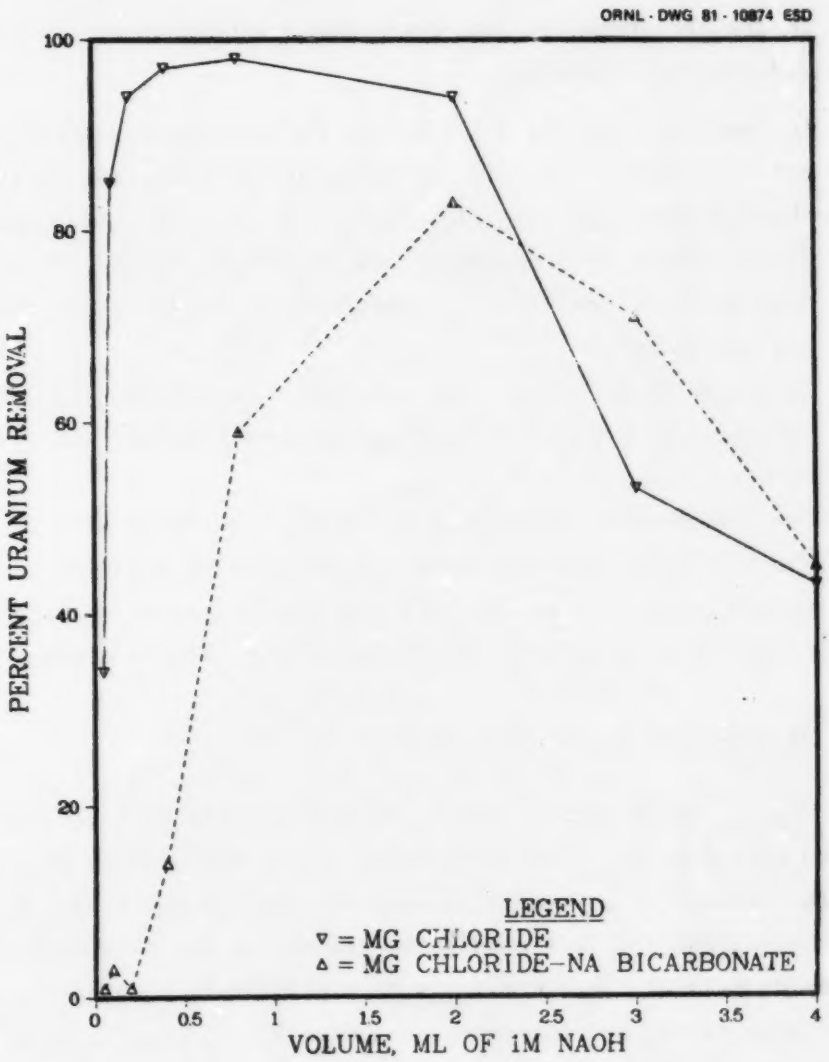

Fig. 2. Percent uranium (initial uranium concentration, 48 µg/L) removed from 5×10^{-3} *M* $mgCl_2$ and from the mixture of 5×10^{-3} *M* $mgCl_2$–5×10^{-3} *M* $NaHCO_3$ solution after addition of varying amounts of 1 *M* NaOH solution.

In the calcium solution, the uranium removal was inconsistent in the pH range 8.5 to 11.5, but it was less than 15%. As the pH of the calcium bicarbonate solution was raised to above 8.7, crystalline $CaCO_3$ was precipitated. The uranium removal from the calcium bicarbonate solution increased with an increase in pH, but the highest value observed was 30% at pH 11.5 (Fig. 1).

The results from the pond water and synthesized water experiments demonstrated the following:

(1) At the higher pH (10.7–11.3), the $Mg(OH)_2$ precipitate played a major role in uranium removal. The presence of excessive carbonate lowered the efficiency of removal. Removal of the hydroxide uranyl form [$(UO_2)_3(OH)_5^+$ or a monomeric analog] by the $Mg(OH)_2$ floc seems to dominate over the uranyl carbonate form, $UO_2(CO_3)_3^{4-}$, but this is not conclusive.

(2) In the pH range between 8.5 and 10.6, the calcium and magnesium carbonate precipitates could remove some uranium, but the efficiencies were very low.

(3) The high removal efficiency by $Ca(OH)_2$ treatment without $MgCO_3$ in the pond water resulted from the presence of indigenous magnesium in the water. Therefore, the magnesium is an essential ingredient to remove uranium from natural waters by lime treatment.

2.2 URANIUM REMOVAL BY COAGULANTS

Most of the municipal water treatment plants have been using coagulation chemicals to remove turbidity, color, and organic matter from the raw waters. The frequently used coagulation chemicals are aluminum sulfate, $Al_2(SO_4)_3$, ferric sulfate, $Fe_2(SO_4)_3$, and ferrous sulfate, $FeSO_4$. Hydroxide sols of these chemicals form positively or negatively charged gelatinous flocs, and the charge and stability of the flocs are pH dependent.

To test the effectiveness of the coagulants for uranium removal, ^{237}U-spiked pond water was prepared in the same manner as the lime-softening experiment. A specified dosage (0.5 to 25 mg/L) of the coagulants was added to 200-mL aliquots of the pond water, and the pH of the solutions adjusted to 4, 6, 8, and 10 using 1 *M* NaOH and HCl in order to determine the optimum dosage and pH for the coagulant treatments. The chemicals used in these experiments were analytical grade. After a 20-min stirring period, each solution was filtered (0.45-μm pore size), and the ^{237}U remaining in solution determined.

2.2.1 $Fe_2(SO_4)_3$ Treatment

As expected, the removal efficiency by ferric sulfate depended upon both the dosage and the equilibration pH of the solution (Table 9 and Fig. 3). The removal percentage increased with increase in dosage, and this trend was more evident in the solutions which had a pH of 6 or 10. There were no considerable differences in uranium removal among the dosages above 10 mg/L at pH 10. At pH 6 and 10, the uranium removal efficiency in the batches containing 25 mg/L ferric sulfate was about 88%, but it was only 40 and 20% at pH 8 and 4, respectively.

2.2.2 $FeSO_4$ Treatment

The experimental results of the ferrous sulfate treatments (Table 9 and Fig. 4) were similar to those of the ferric sulfate treatment in terms

Table 9. Percent uranium removal by $Fe_2(SO_4)_3$, $FeSO_4$, and $Al_2(SO_4)_3$ coagulants with varying pH[a]

Initial pH	Dosage (mg/L)	U removed (%)			Final pH		
		$Fe_2(SO_4)_3$	$FeSO_4$	$Al_2(SO_4)_3$	$Fe_2(SO_4)_3$	$FeSO_4$	$Al_2(SO_4)_3$
4	0.5	7	6	7	4.1	4.2	4.4
	5	14	8	9	4.3	4.2	4.2
	10	8	11	6	3.8	4.1	4.4
	15	13	21	15	4.0	4.2	4.7
	20	17	26	21	4.1	4.2	4.8
	25	18	33	21	4.0	4.1	4.8
6	0.5	16	14	7	6.2	6.1	6.2
	5	43	24	30	6.4	6.0	6.2
	10	63	33	51	6.2	6.1	6.1
	15	76	42	69	6.2	6.2	6.1
	20	84	52	80	6.1	6.2	6.1
	25	89	44	88	6.2	6.2	6.2
8	0.5	1	6	0	8.4	8.1	8.0
	5	4	7	2	8.2	8.1	7.9
	10	17	12	9	7.9	8.1	7.9
	15	21	11	17	8.0	8.1	7.9
	20	33	15	25	7.9	8.0	7.9
	25	43	20	48	7.8	8.0	7.8
10	0.5	1	2	8	10.0	10.1	10.0
	5	27	32	71	10.0	10.0	9.9
	10	83	57	95	9.9	10.0	9.8
	15	86	84	98	10.0	10.0	9.7
	20	80	92	98	9.5	9.9	9.7
	25	87	93	96	10.0	9.9	9.7

[a]Initial U concentration: 83 µg/L.

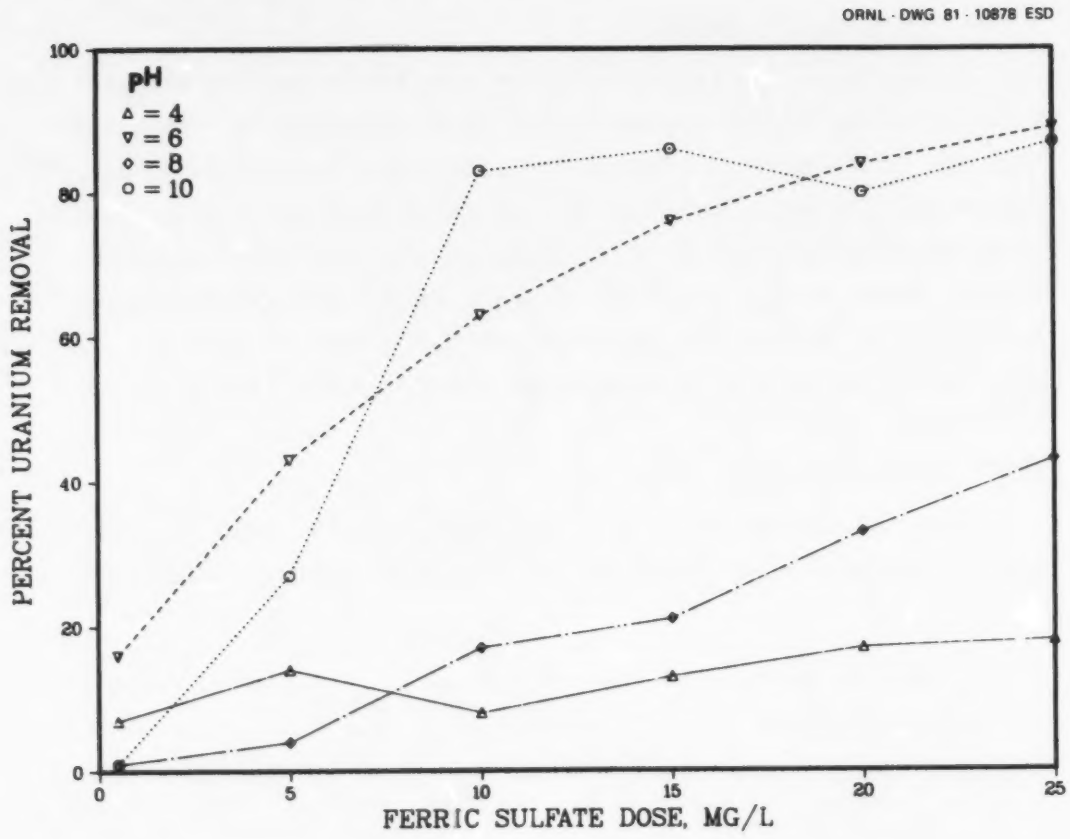

Fig. 3. Percent uranium removed from pond water (initial uranium concentration, 83 μg/L) as a function of doses (mg/L) of $Fe_2(SO_4)_3$ and pH.

of the dependency of uranium removal on pH and dosage. At pH 10, 20, and 25 mg/L, dosages of ferrous sulfate removed more than 90% of the uranium in the solutions. The coagulant was less effective at pH 6, but at pH 6 the removal was higher than at pH 4 and 8.

2.2.3 $Al_2(SO_4)_3$ Treatment

The uranium removal efficiency at pH 10 was 95% with 10 mg/L or higher dosages of aluminum sulfate (Table 9 and Fig. 5). At pH 6 removal increased with increase in dosage, and 87% removal was obtained with a 25 mg/L dosage. On the other hand, only 48% and 21% of removal was obtained at pH 8 and 4, respectively, with the same dosage. These results can be compared to those of 10 mg/L alum addition to the process of the Moffat

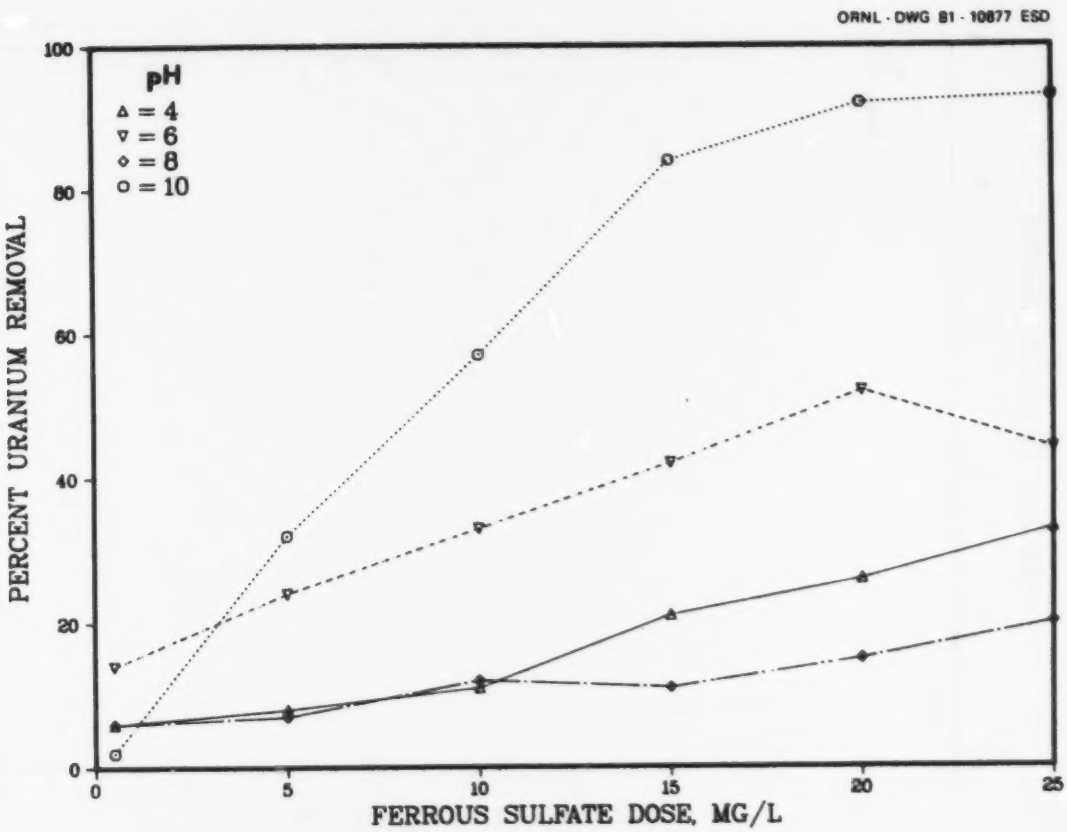

Fig. 4. Percent uranium removed from pond water (initial uranium concentration, 83 μg/L) as a function of doses (mg/L) of $FeSO_4$ and pH.

plant (Denver) discussed in Sect. 1. Under lower alkalinity conditions (Table 5) and near neutral pH, about 75% of the uranium was removed.

2.2.4 Discussion

The physiochemical properties of the hydroxides [$Fe(OH)_3$, $Fe(OH)_2$, $Al(OH)_3$] formed from ferric, ferrous, and aluminum sulfate during the coagulation process are well known. The stability, solubility, and reactivity (adsorption) of the hydroxides are pH dependent. The charge characteristics (zero point of charge of the hydroxides) are different, but the hydroxides have positive charge in the acid range, mixed (neutral) charge at pH 5-7, and negative charge in the alkaline range in general.

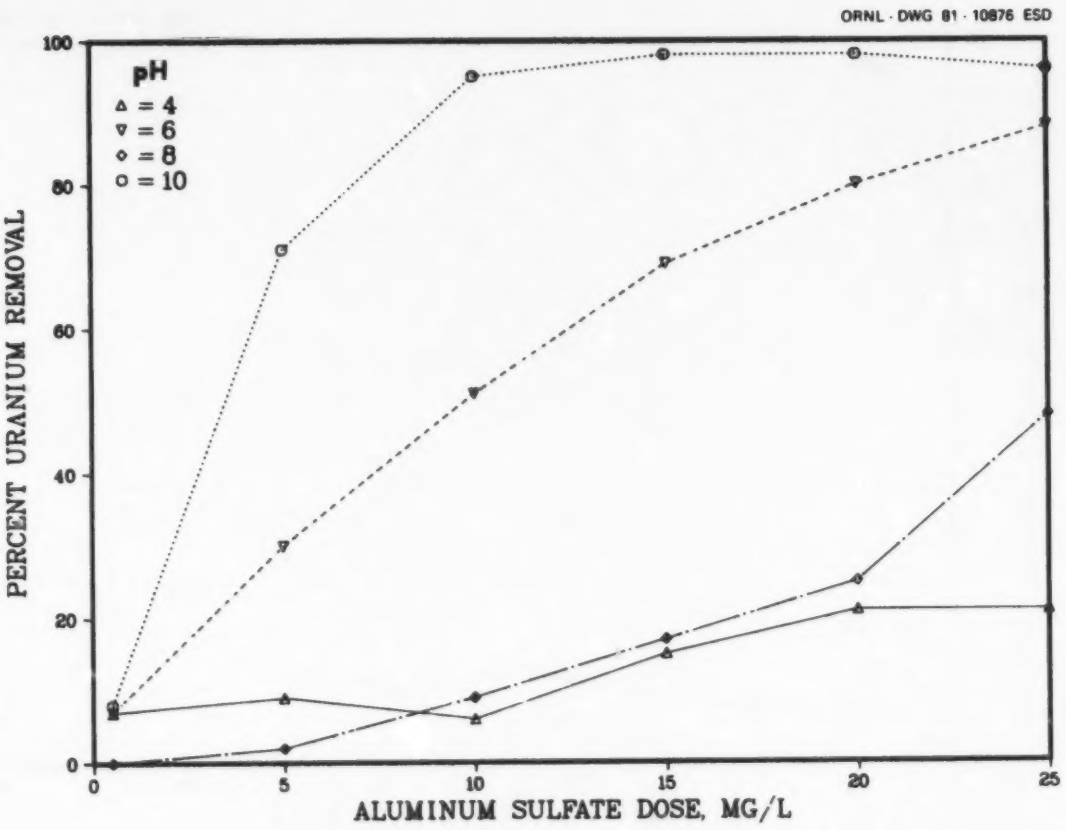

Fig. 5. Percent uranium removed from pond water (initial uranium concentration, 83 μg/L) as a function of doses (mg/L) of $Al_2(SO_4)_3$ and pH.

The pH dependency of the distribution of uranyl species in natural water is also well known.

Positively charged UO_2^{2+} would dominate at pH 4, neutral uranyl carbonate $UO_2CO_3^0$ at pH 6, and negatively charged uranyl carbonates, $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$, at pH 8 and above. At pH 10, the $UO_2(CO_3)_4^{4-}$ species is known to be stable, but $(UO_2)_3(OH)_5^+$ would be a dominant species in carbonate-depleted water. The carbonate in pond water would be depleted by $CaCO_3$ precipitation during the coagulant treatment process.

$$3\ UO_2(CO_3)_4^{4-} + 15\ Ca^{2+} + (Fe, Al)_2\ (SO_4)_3 + 9\ OH^- \rightarrow$$

$$(UO_2)_3(OH)_5^+ + 12\ CaCO_3(s) + (Fe, Al)(OH)_4^- + 3\ CaSO_4 \quad .$$

The pH dependence of the experimental results (Table 9) in uranium removal appears to relate to the uranium species and charges of the coagulant flocs at a given pH. Minimum uranium removal was observed when the charge of the uranyl species was the same as the charge of the flocs, and maximum removal occurred when the charges were opposite or neutral (Table 10).

Although the best results of uranium removal were obtained at the equilibration pH of 10, in practice, the stability of the flocs should be considered. The iron hydroxide is stable in a relatively wide range of pH, but the amphoteric aluminum hydroxide floc is unstable and dissolves at high pH. Therefore, unless coagulant treatment is incorporated with lime treatment, the best results will be obtained at pH 6. A higher dosage (>25 mg/L) of coagulants was required to remove uranium at pH 6 than at pH 10.

2.3 URANIUM REMOVAL BY ADSORBENTS

Many adsorbents such as peat, coal, and hydrous metal oxides have been studied as to their potential for removing uranium from seawater (see Part I of this document). Two of these adsorbents were investigated in this study for removal of uranium from municipal water. Titanium oxide had already been selected for use in a pilot plant to recover uranium from seawater (*Technology Newsletter*, 1980), so it seemed a

Table 10. Suspected uranyl species and charge characteristics of iron and aluminum hydroxide flocs at given pHs of pond water

	Adjusted pH			
	4	6	9	10
Uranyl species	UO_2^{2+}	$UO_2CO_3^0$	$UO_2(CO_3)_2^{2-}$	$(UO_2)_3(OH)_5^+$
Charges of flocs	$(Fe,Al)(OH)_{3-x}^{x+}$	$(Fe,Al)(OH)_3^0$	$(Fe,Al)(OH)_{3+y}^{y-}$	$(Fe,Al)(OH)_{3+z}^{z-}$
Uranium removal (%)[a]	Low (30)	High (88)	Low (48)	High (87)

[a]With 25 mg/L dosage.

likely candidate to study for use in water treatment plants. The adsorption capacity of TiO_2 for uranium from seawater had been studied previously (Ozawa et al., 1979). Activated charcoal is employed as a taste and odor control in many water purification plants, so it was also investigated for removal of uranium. Its usefulness as an adsorbent for uranium had already been demonstrated in neutron activation determinations (Kuleff and Kostadinov, 1978).

Stock solutions of 10^{-2} and 10^{-3} *M* sodium bicarbonate and sodium carbonate were prepared with analytical grade chemicals. The batches containing 200 mL of the stock solution were spiked with ^{237}U, and the pH of the solutions was adjusted with 1 *M* NaOH or HCl solutions. Then, each solution was added to a 250-mL bottle containing one gram of TiO_2 (Baker Chemical Co., Ultrex) or activated charcoal (6-14 mesh, Fisher Scientific Co.). After an overnight equilibration with shaking, the final pH was recorded, each solution was filtered (1.2-μm pore size), and the ^{237}U remaining in the solutions was determined. The free CO_3^{2-} concentration in the solutions was calculated using the final pH in the following relationship:

$$(CO_3^{2-}) = 4.7 \times 10^{-11}(HCO_3^-)/(H^+) \quad .$$

2.3.1 Titanium Oxide (TiO_2)

The uranium adsorption on titanium oxide was influenced by both pH and CO_3^{2-} concentration (Table 11). In the solution with a free CO_3^{2-} concentration of 3×10^{-7} *M* or less, 96% or more of the uranium was adsorbed on the titanium oxide. The pH of the solutions ranged from 5.1 to 6.9. As the free CO_3^{2-} concentration and pH increased, the percent uranium adsorption decreased. At a similar pH (8.3–8.5), as the free CO_3^{2-} concentration increased from 9×10^{-6} *M* to 1×10^{-5} *M* and 1×10^{-4} *M*, the uranium adsorption decreased from 93 to 85 and <1%, respectively.

2.3.2 Activated Charcoal

The results (Table 12) indicated that as pH and CO_3^{2-} concentration in solution increased, the uranium adsorbed on the activated charcoal decreased. At pH 6.4 or lower and free CO_3^{2-} concentration less than

Table 11. Effects of carbonate concentration and pH on the adsorption of uranium on titanium oxide[a]

Initial carbonate concentration (*M*)	Calculated free CO_3^{2-} concentration (*M*)[b]	Final pH	^{237}U adsorbed (%)
0.001 $NaHCO_3$	3×10^{-7}	6.9	96
	9×10^{-6}	8.3	93
	2×10^{-4}	9.7	61
0.01 $NaHCO_3$	6×10^{-8}	5.1	98
	4×10^{-6}	7.0	67
	4×10^{-4}	8.9	<1
0.001 Na_2CO_3	2×10^{-8}	5.5	98
	1×10^{-5}	8.3	85
	2×10^{-4}	9.8	46
0.01 Na_2CO_3	6×10^{-8}	5.1	98
	1×10^{-4}	8.5	<1
	6×10^{-3}	10.5	<1

[a]Solid to solution ratio: 200 mL solution per 1 g TiO_2 (Baker Chemical Co.). Initial uranium concentration: trace ^{237}U ($\approx 2 \times 10^{-6}$ µg/L). Equilibration time: ≈16 h with shaking.

[b]Calculated from measured final pH.

10^{-6} *M*, more than 95% of the spiked ^{237}U was removed from solution by the activated charcoal. On the other hand, at pH 9.1 and 6×10^{-4} *M* CO_3^{2-} concentration, the adsorbed uranium was less than 1%. At approximately the same pH (9.1–9.3), the adsorbed uranium was about 70% in a solution containing 6×10^{-5} *M* of CO_3^{2-}.

Table 12. Effects of carbonate concentration and pH on the adsorption of uranium on activated charcoal[a]

Initial carbonate concentration (M)	Calculated free CO_3^{2-} concentration (M)[b]	Final pH	^{237}U adsorbed (%)
0.001 $NaHCO_3$	7×10^{-6}	7.6	91
	9×10^{-5}	9.3	75
	6×10^{-4}	10.1	39
0.01 $NaHCO_3$	3×10^{-7}	5.8	97
	1×10^{-5}	7.4	75
	6×10^{-4}	9.1	<1
0.001 Na_2CO_3	2×10^{-6}	7.7	92
	6×10^{-5}	9.1	71
	5×10^{-4}	10.4	33
0.1 Na_2CO_3	1×10^{-6}	6.4	96
	1×10^{-5}	7.4	62
	6×10^{-4}	9.1	<1

[a]Solid to solution ratio: 200 mL solution per 1 g activated charcoal (16-14 mesh, Fisher Scientific Co.). Initial uranium concentration: trace ^{237}U ($\simeq 2 \times 10^{-6}$ µg/L). Equilibration time: ≈16 h with shaking.

[b]Calculated from measured final pH.

2.3.3 Discussion

Since most of the raw waters of concern for uranium removal which are received by municipal treatment plants have a pH in the range of 7 to 8, uranium removal by adsorption onto titanium oxide or activated charcoal may be possible if the carbonate concentration is low. Therefore, the sequence of steps in the water purification process becomes very important. Lime additions or other treatments that would affect the

pH and carbonate concentration of the water would also affect uranium removal by adsorption onto titanium oxide or activated charcoal. These materials cannot be considered universal adsorbents. In waters where uranium may be a problem, sorption is likely to be poor (carbonate concentrations may be high).

2.4 URANIUM REMOVAL BY ION EXCHANGERS

Ion exchange resins, particularly anion exchange resins, have been used to recover uranium from uranium mine waters (Ross and George, 1971). The technology has proved to be the most effective and economical recovery method, but most of the existing public water treatment systems do not have such facilities. The application of exchange resins to remove uranium from drinking water would, therefore, be limited to small communities where households treat the raw water through commercially available filtering systems.

2.4.1 Batch Test

To investigate the adsorption of uranium by anion exchange resin, 200-mL batches of the ^{237}U-spiked pond water were adjusted to pH 5, 7, and 9 and then transferred to a 250-mL bottle containing a known amount of resin (50–2000 mg, wet resin weight). After an overnight equilibration with shaking, the solutions were filtered (1.2-μm pore size), and the ^{237}U remaining in each solution was determined.

In most of the batches, 95% of the uranium in the pond water was adsorbed by the anion exchange resin (Table 13). The adsorption of the uranium did not depend on pH or on the carbonate concentration. Low adsorption in the batches with 16 mg of resin did not mean that the exchange sites were saturated with respect to the uranyl species, but that the amount of resin was probably too small to contact all of the available uranyl species in the solution.

To determine the effects of $CaSO_4$ on uranium adsorption by anion exchange resin, varying amounts of resin were added to ^{237}U-spiked 0.001 and 0.01 *M* $CaSO_4$ solutions in the same manner as the pond water.

Table 13. Adsorption of uranium by anion exchange resin from waste pond water at varying pH[a] (Dowex 1-X2, 50-100 mesh, chloride)

Dry resin weight[b] (mg)	Calculated free CO_3^{2-} concentration[c] (M)	Final pH	^{237}U adsorbed (%)
16	1×10^{-8}	5.2	88
165	1×10^{-8}	5.2	89
660	3×10^{-8}	5.6	95
16	9×10^{-7}	7.1	66
165	6×10^{-7}	6.9	96
660	3×10^{-7}	6.6	96
16	1×10^{-4}	9.2	68
165	1×10^{-5}	8.2	96
660	1×10^{-6}	7.2	96

[a]Volume of solution: 200 mL. Initial uranium concentration: 83 µg/L. Equilibration time: ≈16 h with shaking.

[b]Moisture content of resin determined at 105°C: 67%.

[c]Calculated from total carbonate of pond water (1.49×10^{-3} M) and final pH.

The results (Tables 14 and 15) indicate that 98% of the ^{237}U was adsorbed on the resin. Variations in pH and $CaSO_4$ concentration did not influence the efficiency of uranium adsorption by the resin. The results obtained from the batches with 16 mg of resin were inconsistent, probably due to the extremely small solid to solution ratio, which permitted only limited contact of the uranyl ion by the exchange resin.

Similar experiments were conducted to determine the effects of NaCl concentration at different pHs. The results were essentially the same as those for the $CaSO_4$ experiments (Table 16).

Table 14. Adsorption of uranium by anion exchange resin from 0.01 *M* $CaSO_4$ solution at varying pH[a] (Dowex 1-X2, 50-100 mesh, chloride)

Dry resin weight[b] (mg)	Final pH	^{237}U adsorbed (%)
16	5.2	99^+
165	5.8	99^+
660	6.8	99^+
16	6.7	68
165	7.0	99
660	7.3	99^+
16	8.4	98
165	8.4	91
660	8.3	98

[a]Volume of solution: 200 mL. Initial uranium concentration: trace ^{237}U ($\approx 2 \times 10^{-5}$ µg/L). Equilibration time: ≈16 h with shaking.

[b]Moisture content of resin determined at 105°C: 67%.

2.4.2 Column Test

2.4.2.1 Cation Exchange Column

Cation exchange columns in the H^+, Na^+, and Ca^{2+} forms were prepared using Dowex 50-X8, 50-100 mesh (exchange capacity 1.7 meq/mL). The columns contained 5.5 mL resin, 1 cm in diameter and 7 cm in length, and the flow rate was 4 mL per 0.8 cm^2 per min. A total of 2400 mL of ^{237}U-spiked pond water was pumped into the H^+-form column, and each 200 mL of the effluent was collected. The analysis of the effluent batches showed a gradual increase from 3% at the start to 7% of the total ^{237}U activity in the last batch of the effluent. The pH of the effluent was 3.5 and did not change during the elution experiment. The results suggested

Table 15. Adsorption of uranium by anion exchange resin from 0.001 *M* $CaSO_4$ solution at varying pH[a] (Dowex 1-X2, 50-100 mesh, chloride)

Dry resin weight[b] (mg)	Final pH	^{237}U adsorbed (%)
16	52	93
165	6.1	98
660	6.4	98
16	6.6	99
165	6.8	99^+
660	6.8	99^+
16	8.8	82
165	8.5	98
660	7.6	99^+

[a]Volume of solution: 200 mL. Initial uranium concentration: trace ^{237}U ($\approx 2 \times 10^{-5}$ µg/L). Equilibration time: ≈16 h with shaking.

[b]Moisture content of resin determined at 105°C: 67%.

that the uranyl carbonates in the pond water were changed to uranyl cations in the acid resin bed. Removal of uranium by the Na and Ca forms appeared to be low and could be caused by the low selectivity of UO_2^{2+} over Ca^{2+}, Mg^{2+}, and/or by slower dissociation of carbonate from its uranyl complex.

To test this, the pH of the pond water was adjusted to 8.2, 7.0, 5.6, and 4.0 and each solution pumped, in the order of high pH to low pH, into the Ca and Na columns. Neither column removed uranium at pH 8.2 (Table 17). At pH 7 the Ca column did not remove uranium, but the Na column removed about 85%. The Ca column started to remove uranium from the solution at pH 5.6; at pH 4.0, about 60% of uranium in the solution was removed. The Na column continuously removed 70% at solution pHs of 5.6 and 4.0. The pH dependency of the removal process illustrated the

Table 16. Adsorption of uranium by anion exchange resin from 0.02 *M* NaCl solution at varying pH[a] (Dowex 1-X2, 50-100 mesh, chloride)

Dry resin weight[b] (mg)	Final pH	^{237}U adsorbed (%)
16	5.2	85
165	6.0	93
660	6.8	99
16	6.7	84
165	6.9	98
660	7.4	99^{+}
16	7.7	93
165	7.8	99^{+}
660	7.8	99^{+}

[a]Volume of solution: 200 mL. Initial uranium concentration: trace ^{237}U ($\approx 2 \times 10^{-5}$ µg/L). Equilibration time: ≈16 h with shaking.

[b]Moisture content of resin determined at 105°C: 67%.

importance of uranium species in the feed solution on the removal. The difference of removal efficiency between Ca and Na columns suggested that the selectivity order of the cation exchange resin would be $UO_2^{2+} > Ca^{2+} > Na^{+}$ at acid pHs. However, the selectivity of the cation exchange resin for UO_2^{2+} over Ca^{2+}, Mg^{2+}, etc., is probably not large enough to process drinking waters.

2.4.2.2 Elution of Uranium from Cation Exchange Resin

Small plastic columns, 1 cm in diameter and 10 cm in length, containing 7 mL of H^{+}-, Na^{+}-, or Ca^{2+}-saturated cation exchange resin (Dowex 50-X4, 50-100 mesh) were spiked with small amounts of ^{237}U solution. The ^{237}U in the resin columns was eluted with solutions

Table 17. Removal of uranium by Ca- and Na-resin column at varying solution pH[a]

Influent pH	Batch[b] number	Ca-resin column		Na-resin column	
		% Removed	Effluent pH	% Removed	Effluent pH
	1	5	8.2	10	8.4
8.2	2	3	8.2	6	8.4
	3	2	8.3	5	8.4
	4	5	7.2	87	7.3
7.0	5	2	7.2	86	7.2
	6	1	7.2	83	7.2
	7	60	6.1	77	6.3
5.6	8	40	6.0	76	6.1
	9	28	6.0	75	6.1
	10	65	5.1	73	5.7
4.0	11	65	4.3	74	5.4
	12	63	4.2	74	5.2

[a] Initial U concentration: 83 µg/L.

[b] Each batch has 100-mL effluent, and the number was the order of collection.

containing NaCl and $(NH_4)_2CO_3$ (Table 16). The results indicated that 1 *M* NaCl plus 0.1 *M* $(NH_4)_2CO_3$ solution was more effective than 5 *M* NaCl solutions with or without 0.1 *M* $(NH_4)_2CO_3$ for ^{237}U elution from H^+- and Na^+-saturated resin columns. The lower recovery of ^{237}U from Ca^{2+}-saturated resin column could be caused by physical hindrance of calcium carbonate precipitates on the resin surface. It is known that sorbed uranium on cation resin can be quantitatively recovered with 2 to 4 *M* HCl or HNO_3 solution, but the recovery rate is decreased as the acid concentration decreases because of lower selectivity of the resin for H^+ over UO_2^{2+}.

Table 18. Percent uranium recovered from cation resin columns by various eluting solutions[a]

Initial form of U-spiked resin	Eluting solution	Column volume[b]			
		4	8	12	16
H^+	1 *M* NaCl + 0.1 *M* $(NH_4)_2CO_3$	4.5	69.7	88.9	94.0
	5 *M* NaCl	33.3	48.7	50.9	52.5
Ca^{2+}	1 *M* NaCl + 0.1 *M* $(NH_4)_2CO_3$	31.1	33.6	44.3	53.0
	5 *M* NaCl + 0.1 *M* $(NH_4)_2CO_3$	38.1	46.6	56.7	60.9
Na^+	1 *M* NaCl + 0.1 *M* $(NH_4)_2CO_3$	69.6	86.3	92.8	96.4
	5 *M* NaCl + 0.1 *M* $(NH_4)_2CO_3$	51.7	68.6	78.6	82.8

[a] Initial U concentration: trace ^{237}U.

[b] 1-column volume: 7 mL.

In practice, a two-stage column system should be considered to remove uranium from drinking water. In the first stage, one could remove normal hardness in water using a Na^+-saturated resin column. Then UO_2^{2+} in the effluent could be removed after dissociation of complexing anions using a H^+-saturated resin column in the second stage. The used resin columns could be regenerated by NaCl treatment for the Ca^{2+} and Mg^{2+} saturated resin and acid treatment after the NaCl-$(NH_4)_2CO_3$ elution of the UO_2^{2+}-saturated resin. One advantage of this type of dual column is that radium would also be removed. Indeed, such a column would be preferred for the radium plus uranium case. More research needs to be done, however.

2.4.2.3 Anion Exchange Column

An anion exchange column, 1 cm in diameter and 7 cm in length with 5.5-mL column volume, was prepared with carbonate saturated resin (Dowex 1-X2, 50-100 mesh, 0.7 meq/mL resin bed). Fifty liters of the pond water were pumped into the column at a flow rate of 4 mL per 0.8 cm^2 per min. Periodically, 500-mL fractions of the effluent were collected, and uranium alpha activity in the selected effluent batches was determined.

After passing 50 L of the pond water through the column, the uranium remaining in the effluent was less than 1% of the feed solution and did not change throughout the experiment. The results suggested that a much larger quantity of pond water, which would be difficult to handle in the laboratory, would be required to completely load the resin with uranium.

The total uranium retained in the resin column was 4.1 mg (0.083 mg/L U × 50 L × 0.99). Total exchange capacity of the 5.5 mL anion exchange resin was 3.8 meq. Assuming that the dominant uranium species in the pond water is $UO_2(CO_3)_{2.5}^{3-}$ (50% dicarbonato, 50% tricarbonate complex), the milliequivalent weight of the uranium is 79 mg (238 ÷ 3). Therefore, the 5.5 mL resin in the column could adsorb about 300 mg of uranium. These estimates suggest that the column treated with 50 L of the pond water had 1.4% of the resin's capacity saturated with uranium.

To investigate the effect of column dimension and flow rate on uranium removal efficiency by the anion exchange column, two columns (9 and 3 cm in length and 1 cm in diameter) were tested with varying flow rates of ^{237}U-spiked pond water (Table 19). In all cases, more than 99% of the uranium in the pond water was removed by the carbonate-saturated anion exchange resin.

2.4.2.4 Uranium Loading Capacity of Anion Exchange Resin

The apparent failure to evaluate maximum uranium loading with the pond water prompted another attempt with a smaller column and a higher

Table 19. Uranium adsorption by two different anion exchange columns with varying flow rate of ^{237}U-spiked pond water[a]

Column length (cm)	Flow rate, mL per 0.785 cm^2 per min			
	1	3	6	12
3	99	99	99	99
9	99	99	99	99

[a]Uranium concentration: 83 µg/L.

uranium concentration in the feed solution. The column was 3.6 cm long and 0.4 cm in diameter with 0.5 mL resin volume. The ^{237}U-spiked feed solution had 23.8 µg/mL (10^{-4} *M*) ^{238}U, 10^{-2} *M* $(NH_4)_2CO_3$; the flow rate was 5 mL per 0.1 cm^2 per min. The calculated loading capacity of the 0.5 mL resin (Dowex 1-X8) was 48 mg of uranium if the uranium in the solution was $UO_2(CO_3)_{2.5}^{3-}$ form.

A gradual increase in the uranium concentration in the effluent solution was observed (Table 20 and Fig. 6). The uranium in the effluent was 1% of the initial concentration up to when 400 mL of the feed solution had passed through the column. At this point, 20% of the calculated capacity of the resin was saturated with uranyl carbonate. When the column processed 1300 mL of the feed solution, the effluent contained 10% of the initial concentration, and 65% of the resin capacity was saturated. When 1800 mL of the feed solution passed through the column, 81% of the resin was saturated with uranyl carbonate, and 28% of the uranium in the feed solution was in the effluent solution (Table 21). The experimental data curve (Fig. 6) appears to fit an exponential curve, $y = be^{mX}$, where y = percent uranium remaining in effluent, b = 0.79 as the intercept on y, and m = 0.002 as the slope with correlation coefficient (r) = 0.99.

Table 20. Removal of uranium by a 0.5-mL anion resin column[a]

Volume of effluent (mL)	Uranium in effluent (%)	Volume of effluent (mL)	Uranium in effluent (%)
100	1.0	1000	5.7
200	1.0	1100	6.7
300	1.0	1200	8.3
400	1.0	1300	9.7
500	2.2	1400	12.5
600	2.6	1500	15.6
700	3.1	1600	18.1
800	3.8	1700	22.9
900	4.5	1800	28.5

[a]Feed solution had 23.8 mg/L (10^{-4} *M*) of uranium and 10^{-2} *M* $(NH_4)_2CO_3$.

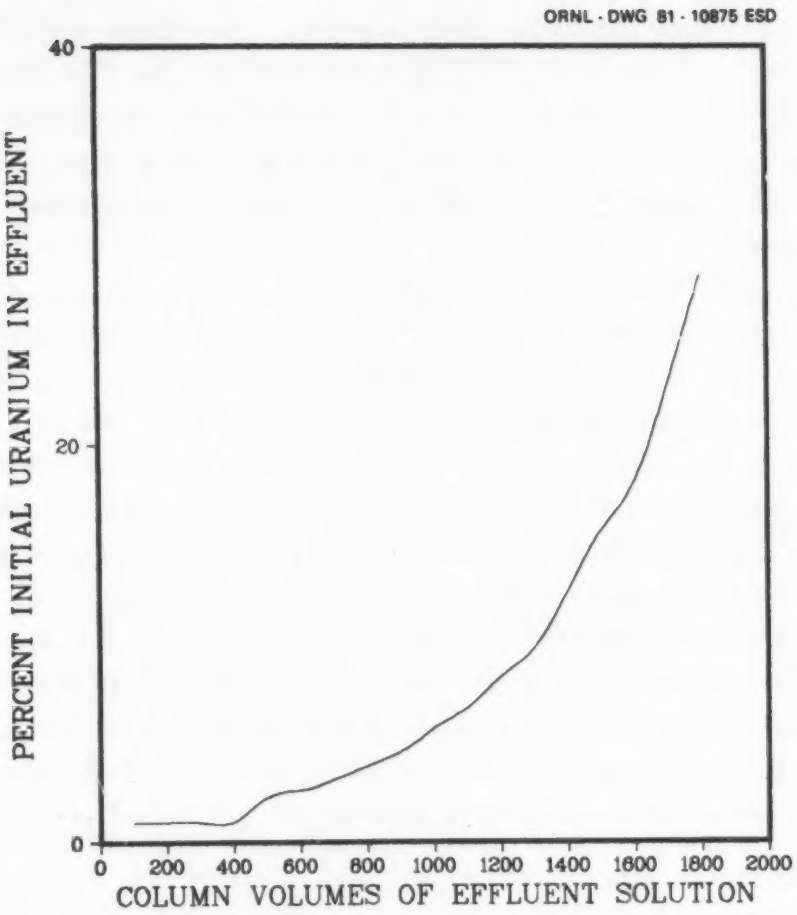

Fig. 6. Percent uranium (initial uranium concentration, 23.8 mg/L) passed through an anion exchange column versus cumulated column volumes of influent solution.

2.4.2.5 Elution Experiment of Anion Exchange Resin

The same column used for the loading experiment (Table 20) was eluted with 1.0 *M* NaCl–0.5 *M* $NaHCO_3$ solution. This column contained 39 mg of uranium (Table 21); about 28% of the uranium in the column was eluted with four column volumes (2 mL) of the solution, 60% with 14 column volumes, and 85% with 40 column volumes of the eluting solution (Fig. 7). The remaining 15% remained with resin.

In a separate experiment, uranyl carbonate-treated anion exchange resin columns were eluted with solutions having various compositions (Table 22). The solutions containing 1.0 or 1.5 *M* NaCl and dilute carbonate had the highest efficiency.

Table 21. Percent of uranium loading on resin column at the selected uranium concentration in the effluent

Volume of effluent (mL)	U in effluent (%)	U in resin column (mg)	Loading of resin column (%)
400	1.0	10	20
1300	9.7	31	65
1800	28.5	39	81

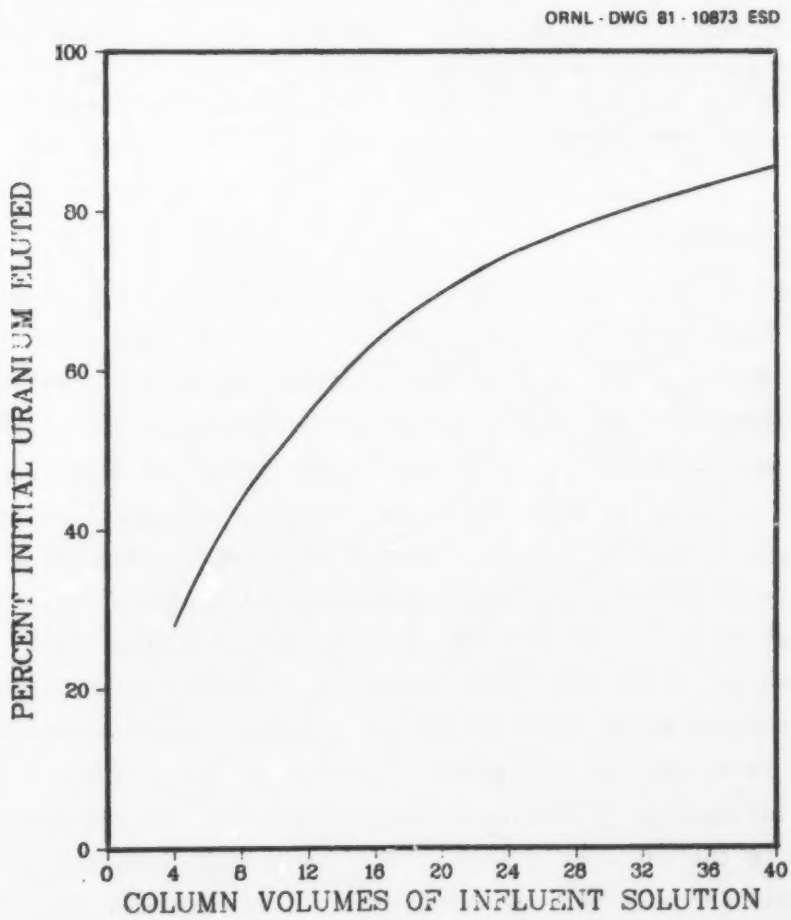

Fig. 7. Percent of uranium eluted from uranium-containing anion exchange column (initial uranium loading, 39 mg) by 1.0 *M* NaCl– 0.5 *M* $NaHCO_3$ solution versus cumulated column volumes of elution solution.

Table 22. Percent ^{237}U recovered from anion resin columns by various eluting solutions

Eluting solution	Column volume[a]			
	1.5	3	4.5	6
1.5 *M* NaCl + 0.1 *M* $(NH_4)_2CO_3$	57.8	82.2	90.8	94.8
1.5 *M* NaCl + 0.5 *M* $NaHCO_3$	52.6	76.0	83.7	88.9
1.5 *M* NaCl + 0.1 *M* $NaSO_4$	49.1	72.4	81.7	85.5
1.5 *M* NaCl + 0.5 *M* $NaSO_4$	49.3	73.1	81.5	85.2
1.0 *M* NaCl + 0.5 *M* $NaHCO_3$	50.0	75.3	90.2	95.1
1.0 *M* NaCl + 0.1 *M* $(NH_4)_2CO_3$	42.1	74.4	84.7	90.1
5.0 *M* NaCl + 0.1 *M* $(NH_4)_2CO_3$	35.8	49.7	57.6	64.6
5.0 *M* NaCl + 0.01 *M* $(NH_4)_2CO_3$	37.4	52.6	62.2	68.7

[a] 1 column volume = 7 mL.

2.4.3 Discussion

Both batch and column results confirmed that the strong base anion exchange resin has a very large adsorption capacity and selectivity for uranyl carbonates, which are common chemical species of uranium in surface and groundwaters. The uranyl carbonate adsorption on the resin column depends on flow rate, pH, and concentration of uranyl carbonate and other competing anions. At relatively high uranium concentrations ($\sim 10^{-3}$ *M*) of influent solutions, loading capacity of a resin column at a point of 5% leakage in effluent decreased with increasing flow rate and carbonate concentration ($\sim 10^{-1}$ *M*) (Shankar, Bhatnagar, and Murthy, 1956). The study also found that the loading capacity decreased with decreasing uranium concentration, indicating that a bigger column volume would be required to obtain the same percent leakage in the effluent from a diluted influent as from a more concentrated one. In the presence of vanadium in the influent solution, uranium loading capacity of anion resin would decrease because vanadium would be held much more strongly by the resin (Grinstead, Ellis, and Olson, 1956). Using a relatively large anion resin column with flow rate 100 L per 1000 cm^2 per min, Ross and George (1971) were able to remove 98% of uranium from mining solution

containing 4×10^{-5} *M* uranium. Total loading of uranium at the 2% leakage point was 50% of the theoretical resin capacity.

The loading experiment of this study (Table 21) with 10^{-4} *M* uranium and 10^{-2} *M* $(NH_4)_2CO_3$ solution and a flow rate of 5 mL 10.1 cm^2/min showed that at 20% loading the uranium leakage was 1%, and at 65% loading the leakage was 10% of the uranium concentration in the influent solution.

An extrapolation of the above results, obtained from relatively concentrated uranium systems, to an extremely diluted system such as the pond water or surface water and groundwater may or may not be valid, but there are no other ways to determine the loading capacity and leakage concentration for the diluted system without site-specific field experiments. The pond water had 3×10^{-7} *M* uranium, 10^{-3} *M* HCO_3^-, and $<10^{-4}$ *M* of other anionic species (Table 4). The raw waters used for the municipal water plant have 10^{-7} to 10^{-9} *M* of uranium. In general, the molar ratio of uranium to total anionic species in natural waters is $1:10^5$, and most of the laboratory loading (literature) studies were conducted with a ratio between $1:10^2$ and $1:10^3$. The low uranium concentration and high anion concentration in natural waters could reduce the efficiency of uranium removal by anion exchange column.

For estimation purpose, a very conservative value (10% maximum loading with 1% uranium leakage) was selected. A commercial demineralizer (Cole-Parmer, Cat. No. C-1503, flow rate, 2 gal/min) could hold 4400 mL (5 lb) of anion exchange resin. The 10% loading capacity for $UO_2(CO_3)_{2.5}^{3-}$ of the demineralizer is equivalent to 21.12 g of uranium. The demineralizer could, therefore, process 2.6×10^5 L of the pond water (0.08 mg/L of uranium) with <1% leakage equivalent to <0.8 µg/L of uranium in the effluent. If a water has 0.01 mg/L, the demineralizer would process 2×10^6 L of the water and the uranium concentration of effluent would be 0.1 µg/L. The list price of the demineralizer was $108, and the price of replaceable anion exchange resin was $60 per 5 lb (no endorsement of the Cole-Parmer unit is intended). The gamma dose rate at one meter for ^{234}Th, ^{234}Pa, and ^{234}U can be calculated assuming a point source. Thus 1 g of ^{238}U (in equilibrium with ^{234}U in the water) on an anion column would result in an annual dose of 0.02 mrem (natural background is near 100 to 200 mrem/year).

The recovery rate of uranium from anion resin columns by eluting solutions was relatively low; less than 60% was eluted with 1.5-column volumes of the solutions. Under the best conditions, 90% was recovered with elutions of 4.5 column volumes. The elution efficiency could be improved by increasing retention time of the solution on the resin. Ross and George (1971) were able to recover 98% uranium from 50% saturated resin using 1.9 column volumes of 1.1 *M* NaCl–0.05 *M* $NaHCO_3$ solution at a resin retention time of 3.5 h. Since the elution efficiency would also depend on the column loading and if the anion exchange process would be considered as one of the options for municipal water treatment, further detailed studies should be conducted. For the household-type demineralizer column, recycling the resin by users may not be practical.

2.5 URANIUM REMOVAL BY REVERSE OSMOSIS

Reverse osmosis (RO) water treatment systems are generally effective for the removal of most inorganic species in feed waters (Sorg and Logsdon 1980). A study of RO performance in the separation of uranium from synthetic mine solutions indicated that the RO system with cellulose acetate membranes was highly effective (above 96% rejection rate) in the uranium sulfate concentration range of 100 to 800 mg/L in feed solutions (Sastri and Ashbrook, 1976). The performance of the RO system would, however, depend on membrane material, system construction, operation condition, feed solution composition, etc.

In this experiment, the uranium removal efficiency of an RO system was examined using a commercial cellulose acetate membrane module (2-in. deep by 24-in. long, membrane area 11 ft^2, Cole-Parmer Instrument Co., Cat No. C-1501-90). A cylindrical plastic compartment (2.3 in. deep by 24 in. long) for the module and feed solution was fabricated. The flow rate of effluent through the membrane was 0.3 gal/h and was regulated by N_2 gas pressure (20 psi).

About 4 L of prefiltered (Whatman No. 42) pond water containing 83 µg/L uranium passed the RO membrane unit. Then 1.5 L of ^{237}U-spiked pond water was put through the unit. Five 200-mL aliquots were collected successively after discarding the first 500 mL of the effluent of the

spiked pond water. The results (percent removal) of spiked ^{237}U and indigenous ^{238}U from the feed solution are given in Table 23.

The percent uranium removal (rejection rate by the RO unit) decreased as the filtration progressed. Although the removal of uranium was high (>90%) for the first 4 L (data not shown but inferred from initial collection data, Table 23), apparently only about 5 L can be treated at close to 90% removal with this design. This is not as satisfactory as the anion exchange resin column. Since a principal objective of this test was to evaluate the potential of the method, the capacity is not a factor, and it can be concluded that RO can remove uranium to below 90% of influent concentrations and, therefore, is a viable option for treatment purposes.

Table 23. Percent of uranium removed by a reverse osmosis module

Fraction of effluent collected (mL)[a]	^{237}U removed (%)	^{238}U removed (%)
500-700	93	94
700-900	87	91
900-1100	87	85
1100-1300	85	85
1300-1500	79	86

[a]An initial 4 L was passed prior to the initiation of sample collection after the introduction of ^{237}U into the source water.

3. SUMMARY OF RESULTS

The total dissolved uranium concentration in the water samples provided by 20 public water supplies was in a range from 0.1 to 9.1 µg/L. The pHs of the raw and treated waters were between 7.4 and 9.5. The lack of noticeable differences in uranium content among raw water, intermediate stage, and product water samples indicated that municipal water treatment practices are not effective in removing uranium. Supplementary work suggested that the treatment conditions established for the reduction of turbidity and hardness by municipalities are not optimum for the removal of uranium.

Batch tests of water softener, $Ca(OH)_2$, showed that lime treatment alone could reduce uranium concentrations of the tested water (83 µg/L uranium) by 85 to 90% at pH between 10.6 and 11.5. The removal efficiency was improved up to 99% by the addition of $MgCO_3$ to the water. Uranium was removed from solution by coprecipitation with $Mg(OH)_2$ and $CaCO_3$. In practice, treatment of hard water may not need additional $MgCO_3$, but the $MgCO_3$ addition would be needed for the treatment of soft water. Individual plant water composition will need to be considered.

Coagulants [$Fe_2(SO_4)_3$, $FeSO_4$, $Al_2(SO_4)_3$] removed 85% or more of the uranium from solution containing 83 µg/L uranium at pH 6 and 10 with a 25-mg/L dose. At pH 8, the removal efficiency was less than 50%. The pH dependency in uranium removal appears to be related to the uranium species and charges of coagulant at a given pH from 4 to 10. Since most municipal water treatment plants were using water softener and/or coagulant, the treatment pH above 10 with $Fe_2(SO_4)_3$ would be more effective than pH 6 for uranium removal. Total alkalinity is the important variable and actual removal will be water specific. The adsorbents titanium oxide and activated charcoal also removed more than 90% of uranium in solution at pH <7 and <7.5, respectively. Excess carbonates in the solution reduced the adsorption efficiency of the absorbents. Application of the adsorbents is a possible option, but it will require additional treatment costs if added to existing treatment systems.

Strong base anion exchange resin was the most effective and universal adsorbent for uranyl carbonates, which are common chemical species in

natural water. Excess carbonates and polyanion species (V, Mo, etc.) in water would reduce the removal efficiency of the resin. Although about 10% of adsorbed uranium was remaining with resin after elution with 1.1 *M* NaCl + 0.01 *M* $NaHCO_3$ solution, the resin could be recycled for water treatment or washed with dilute acid after carbonate removal. The anion exchange technology for a large volume of water treatment is available but will require large capital investment. Small anion exchange columns should be considered, however, to remove uranium from private wells located in uraniferous strata. A column containing 5 lb of anion exchange resin could treat, for example, 10^6 L of water containing 83 µg/L uranium with less than 1% leakage (0.8 µg/L uranium in effluent). An efficient removal would be expected on lower uranium waters.

The reverse osmosis system could remove uranium from the pond water, but the removal efficiency decreased to 79% as the filtration progressed. The results also indicated that our RO system could treat only about 5 L of the pond water at close to 90% removal rate. A commercial laboratory RO unit (Cole-Parmer Instrument Co., Cat. No. C-1501-40, $1582/unit) was claimed to produce better than our results in terms of the salt removal rate. Direct comparison of the RO performance with other treatment methods is difficult because each of the methods has advantages and disadvantages. However, RO will work to lower uranium concentrations, and it is a viable option, recognizing the large water losses involved in the reject stream. Where other contaminants are involved, RO may be the favored option because of simplicity of use.

4. RECOMMENDATIONS

The results presented in this report represent bench-scale testing on a natural water of a quality representative of uranium-bearing waters (Ca, Mg, carbonates). The application of coagulants and/or softeners for uranium removal is possible, generally requiring lowering or raising the natural pH from the 7 to 8 region where uranium is most stable. The amount of Ca, Mg, and carbonates in the feed water will influence the magnitude of removal. For example, Table 2 of Part I showed that by simply raising the pH of several of the municipal waters received for uranium analysis, variable amounts of uranium were removed. This was most likely caused by the amount of magnesium present (cannot be substantiated).

Anion exchange resins will be useful for removing uranium. On a small scale, disposable cartridges may be employed. For reusable resin (larger scale treatment) some problems with uranium elution are anticipated and will need either acid stripping or resin replacement.

5. REFERENCES

Brits, R.J.N., and M.C.B. Smit. 1977. Determination of Uranium in Natural Water by Preconcentration Anion-Exchange Resin and Delayed-Neutron Counting. Anal. Chem. 49(1):67-69.

Grinstead, R. R., D. A. Ellis, and R. S. Olson. 1956. Recovery of Uranium from Sulfuric Acid and Carbonate Leach Liquors by Anion Exchange. In: Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Vol. 8, United Nations, New York. pp. 45-53.

Haggag, A. M., and T. R. Stokely. 1981. Oak Ridge National Laboratory, Oak Ridge, Tennessee. Personal communication to S. K. Hall, Oak Ridge National Laboratory.

Hodge, V. F. 1975. Semi-Quantitative Determination of Uranium, Plutonium, and Americium in Sea Water. Anal. Chem. 47(11):1866-1868.

Kuleff, I., and K. N. Kostadinov. 1978. Epithermal Neutron-Activation Determination of Uranium in Environmental Waters by Np-239 After Preconcentration on Activated Carbon. J. Radioanal. Chem. 46(2):365-371.

Langmuir, D. 1978. Uranium Solution – Mineral Equilibria at Low Temperatures with Applications to Sedimentary Ore Deposits. Geochim. Cosmochim. Acta 42:547-569.

ORNL-2557. 1959. Report of the Joint Program of Studies on the Decontamination of Radioactive Waters. Health Physics Division, Oak Ridge National Laboratory, and R. A. Taft, Sanitary Engineering Center, Public Health Service. Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Ozawa, Y., T. Murata, H. Yamashita, and F. Nakajima. 1979. Uranium Extraction from Sea Water with Composite Hydrous Titanium (IV) – Iron (II) Oxide. J. Nucl. Sci. Technol. 16(9):671-678.

Ross, J. R., and D. R. George. 1971. Recovery of Uranium from Natural Mine Waters by Countercurrent Ion Exchange. U.S. Bur. Mines Report RI-7471. 17 pp.

Sastri, V. S., and A. W. Ashbrook. 1976. Reverse Osmosis Performance of Cellulose Acetate Membranes in the Separation of Uranium from Dilute Solutions. Sep. Sci. 11(4):359-374.

Shankar, J., D. V. Bhatnagar, and T.K.S. Murthy. 1956. An Ion Exchange Process for the Recovery of Uranium from Carbonate Leach Solutions. In: Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Vol. 8, United Nations, New York. pp. 64-70.

Sorg, T. J., M. Csanady, and G. S. Logsdon. 1978. Treatment Technology to Meet the Interim Primary Drinking Water Regulations for Inorganics: Part 3. J. Am. Water Works Assoc. 70(12):680-691.

Sorg, T. J., and G. S. Logsdon. 1980. Treatment Technology to Meet the Interim Primary Drinking Water Regulation for Inorganics: Part 5. J. Am. Water Works Assoc. 72(7):411-422.

Technology Newsletter. 1980. Japanese Will Step Up Efforts to Recover Uranium from Sea Water. Chem. Week 126:42.

Thompson, C. G., J. E. Singley, and A. P. Black. 1972. Magnesium Carbonate: A Recycled Coagulant. J. Am. Water Works Assoc. 64(1):11-19.

Weissbuch, H., A. Cotrau, and P. Velicescu. 1969. Removal of Dissolved Radioactive Elements from Water by Treatment with Flocculating Agents. Z. Gesamte Hyg. Ihre Grenzgeb. 15(10):761-763.

APPENDIX

Methods of Sample Preparation and Uranium Analysis for Municpial Water Samples

Equipment

An anion exchange column was constructed by connecting a 125-mL cylindrical glass separatory funnel with Teflon valve and tubing to a polyethylene insert (8 mm ID, 18.5 mm long), a small capsule specially constructed to fit inside an irradiation vial. Five holes (0.34 mm) had been drilled into the bottom of the insert to allow passage of the sample solution into a 250-mL filtering flask which was connected with rubber tubing to a vacuum pump. A valve inserted into the tubing between the filtering flask and the vacuum pump allowed the pressure to be adjusted. Whatman No. 50 filter paper, cut to fit the inside of the insert, was placed on the bottom of the insert and also on top of the resin in the insert to discourage displacement of the resin.

Reagents

An ammonium carbonate stock solution (1.3 *M*) was passed through an anion exchange resin column in order to reduce any uranium contamination. A portion of this stock solution was used to make up a wash solution which was 0.1 *M* in ammonium carbonate and 20% in methanol. All subsequent dilutions were mixed from the decontaminated stock solution. Dowex 1-X8 (50–100 mesh, Bio·Rad Laboratories, Richmond, California) anion exchange resin in chloride form was used to preconcentrate the uranium from the sample solutions. The resin was converted to carbonate with 1 *M* $(NH_4)_2CO_3$, stored in a solution which was 0.1 *M* in ammonium carbonate and 20% in methanol. Although no uranium was detectable in the amount of resin used, an initial acid washing step before the carbonate conversion would be advisable.

Procedure

A 100-mL portion of each sample was transferred in a disposable beaker to a separatory funnel which had been prewashed with 0.1 *M* HNO_3

and rinsed with deionized water. The sample solution was made 20% in methanol and 0.1 *M* in ammonium carbonate, bringing the total solution volume to 130 mL. The polyethylene insert was connected to the filtering flask with a small piece of tubing and filled with approximately 0.8 mL of resin. Another piece of tubing was attached to the top of the insert and filled about three-fourths full with wash solution before being connected to the separatory funnel. Then the valve to the separatory funnel was opened and the sample solution allowed to filter through the resin at atmospheric pressure. Air bubbles could usually be removed by pressing on the tubing. When the flow rate slowed, a vacuum was applied. By adjusting the stopcock in the vacuum line, a maximum flow rate of 4 to 6 mL per minute was maintained. When all of the sample solution had passed through the resin, the separatory funnel was rinsed thoroughly with approximately 10 mL of wash solution. Air was then drawn through the insert for a couple of minutes before the vacuum pump was disconnected, and the insert was capped and dried under vacuum for a minimum of 2 h.

To demonstrate the efficiency of the experimental setup in removing uranium from the water, 100-mL aliquots of several of the water samples received were spiked with a known amount of ^{237}U, the methanol and ammonium carbonate were added, and then the sample solution was passed through the resin column. The ^{237}U adsorbed on the resin was determined by gamma counting with a thallium-activated NaI scintillation crystal and dual photomultiplier tube detection system. A standard of the same geometry was prepared by spiking some of the resin in an insert with the same amount of ^{237}U. The water samples tested were representative of all the samples received. The lowest recovery obtained was 73%, but a second analysis of another 100-mL aliquot of the same sample yielded 99%. Two other samples showed 81 and 83% recovery, respectively, and on duplicate runs, the recoveries were 99%. This variability in the recovery could be due to the differences in flow rate or channeling in the resin bed, both of which would affect the contact of the solution with the resin beads and thus the uranium retention by the column. The inconsistencies were therefore more likely due to handling errors rather than to being sample-derived problems in resin sorption. To ensure meaningful results,

most raw and final water samples were replicated, usually at an interval of a week or so.

Controls consisting of 100 mL of deionized water instead of sample solution were run at intervals during the analyses to ensure that the equipment remained free of any contamination. The equipment was cleaned with 0.1 *M* HNO_3 between samples and rinsed thoroughly with deionized water. As a check on the reproducibility of the system, duplicate runs were made on most of the raw water samples. If variability occurred among these runs, the runs were repeated until consistent results were obtained. Measurements of pH were also recorded for each sample.

Two problems became apparent at the beginning of the analyses. First, Dowex 1-X2 (50–100 mesh) anion exchange resin swelled out of the insert during the uranium preconcentration step, but a resin with greater cross linkage, Dowex 1-X8 (50–100 mesh), was substituted and the problem eliminated. Second, in some of the sample solutions, cloudiness developed upon addition of the ammonium carbonate solution. A white precipitate settled out onto the sides and bottom of the separatory funnel if the solution was allowed to set. The solutions which precipitated were filtered through a 0.22-μm filter before passing through the resin. Analysis of the filter paper showed that very little uranium was incorporated into the precipitate.

After the preconcentration step, the insert with the uranium-loaded resin was placed in an irradiation vial. Then, neutron irradiation of each sample was performed in the neutron activation analysis laboratory at the Oak Ridge Reactor located at the Oak Ridge National Laboratory. Irradiations were performed for 60 s at a flux of 3.97×10^{13} $n/cm^2/s$. The sample was then transferred to a neutron counter, and counts were taken after a delay of 6 s. Calibration was done directly with uranium standards. The spectrum was processed with a PDP-15 computer, using the MONSTR program which translates the data collected into the corresponding uranium concentrations.

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